# BLOCH EQUATIONS FOR A HYDROGEN-BONDED FERROELECTRIC*

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Using the information about the critical slowing down of the polarization of a hydrogen bonded ferroelectric, the simplest kinetic equations describing the critical kinetic in so-called classical region of the phase transition are derived. The restrictions imposed by symmetries of the KDP are studied. The obtained kinetic equations are less symmetric, exact counterparts of the phenomenological Bloch equations. The response functions obtained from the kinetic equations reveal the existence of the overdamped soft modes.

## 1. Introduction

It is well-known that the set of equations proposed by Bloch form the basis for the experimental and theoretical studies of paramagnets. Various examples of the applications of these equations can be found in the famous book by Abragam (1961). This set of equations is extensively used for description of other systems, in which one does not deal with the proper magnetic moments but uses some dichotomic variables. The famous example is the photon echo in an ensamble of atomic systems discussed by Kurnit et al. (1966). Since the hydrogen-bonded ferroelectrics are described in terms of the pseudo-spin operators, it is tempting to use Bloch equations for description of the electric and critical properties of such ferroelectrics. Such attempts are recently reviewed in the paper by Blinc and Žekš (1974). They also shown that the response functions, which can be obtained from Bloch equations, reveal the existence of both the soft modes and the central peak. These features are observed in experimental studies.

However, it was recently realised that even if one can use the set of Bloch-like equations, their actual form depends strongly on symmetries of a considered system (cf. Götze and Michel (1974)).

Differently then paramagnets, the most famous example of a hydrogen bonded ferroelectric — the KDP crystal — possesses lower symmetry (cf. Moore and Williams

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(1972)). Besides, the interactions between electric dipoles are strongly anisotropic, much more than in paramagnets.

Additionally, Bloch Equations describe a strongly polarized paramagnet, whereas in the case of a ferroelectric, one tries to describe the fluctuations of the polarization of an unpolarized sample.

The purpose of our paper is to study the influence of the peculiarities of KDP crystals on the form of Bloch Equations. Following Götze and Michel (1974), we derive the formula for polarization response function. From this formula we derive the Bloch-like equations, which are indeed different from those derived by Blinc and Žekš (1972). They derive these equations from Bloch Equations valid for paramagnets.

In principle, one can include the influence of other degrees of freedom, such as the lattice vibrations. This is a trivial task if the lattice is treated as a thermal bath. If part of the lattice forms an independent subsystem, the problem is more complicated, and the system is described not only with the help of components of pseudospin, but also with some densities of conserved lattice variables, as in the model proposed by Cowley and Coombs (1973). For simplicity we will discuss mainly the response to a spatially homogeneous field. In such a case the energy flow is not excited by an external field.

## 2. *The response function*

Let us consider a system of $N$ particles contained in the volume $V$. Denote the Hamiltonian of this system by $H$. If this system is placed into an external time dependent field of a strength $\mathscr{F}(t)$ it produces the disturbance, which may be represented by addition of the term

$$H_1(t) = -B^+\mathscr{F}(t) \tag{1}$$

to the Hamiltonian of the system. $B^+$ is the operator representing the variable coupled to the external field. Denote the change of the mean value of any variable $A$ describing the considered system, under the influence of an external field by $\Delta\langle A\rangle(t)$. In the approximation linear in the strength $\mathscr{F}(t)$, the Fourier transform of this change is given by

$$\Delta\langle A\rangle(\omega) = \chi_{AB}(-\omega)\mathscr{F}(\omega). \tag{2a}$$

The Fourier transform is defined as

$$\mathscr{F}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, e^{i\omega t}\mathscr{F}(\omega)$$

and the mean value is calculated in thermodynamic limit $N \to \infty$, $V \to \infty$, $N/V = \text{const}$, which we will denote by Lim. The actual form of the susceptibility $\chi_{AB}(\omega)$ depends on the condition of the measurements. This fact is formulated with the help of initial (or boundary) conditions imposed on Liouville's equation as it was shown by Kalashnikov (1974). In Kubo's formulation one considers the response of the system being initially in the contact with the thermal bath, then decoupled from it, and finally disturbed by an external field. This procedure yields the well-known response function of an isolated system. It is well-known that in Kubo's theory of linear response, the static susceptibilities are generally incorrect. To improve this fault of Kubo's theory, Kalashnikov (1974) considered the system being in contact with reservoires. These contacts induce thermal flows in disturbed system, and these flows in turn change the quasi-static response. Flows in a system are connected with a set of slowly-varying in space and time variables (gross-variables). Kalashnikov's results seem to be correct only when one considers the changes of the mean values of gross-variables under the influence of a field also coupled to a gross--variable.

The Kalashnikov formula for the dynamical susceptibility reads

$$\chi_{AB}(\omega) = \chi_{AB} + i\beta\omega G_{AB}^{\text{isoth}}(\omega), \tag{2b}$$

where $\beta$ is the inverse temperature of the thermal bath. The proper isothermal static susceptibility is defined in terms of scalar product. For extensive variables $A$, $B$ one has

$$\chi_{AB} = \text{Lim}\,\frac{1}{N^2}\langle A, B\rangle.$$

In Kalashnikov's theory the scalar product $\langle , \rangle$ is defined as Kubo's correlator

$$\langle A, B\rangle \equiv \beta\int_0^1 d\tau\, \text{Tr}\, A\varrho_0^{\tau}(\Delta B)^{+}\varrho_0^{(1-\tau)}, \tag{3}$$

where

$$\Delta\langle B\rangle = B - \langle B\rangle_0, \qquad \langle B_0\rangle = \text{Tr}\, B\varrho_0$$

and $\varrho_0$ is the density matrix of the equilibrium state. The scalar product $\langle , \rangle$ has the following properties

$$\langle A, A\rangle \geqslant 0, \qquad \langle A, B\rangle = \langle B^{+}, A^{+}\rangle, \qquad \langle A, B\rangle^{*} = \langle B, A\rangle \tag{4}$$

and is linear in the first argument. Additionally one has

$$\langle A, B\rangle = \langle \Delta A, B\rangle.$$

The scalar product allows us to introduce the Hilbert space of variables, which we shall denote by $\mathscr{H}$. In this Hilbert space, Liouville's operator $\mathscr{L}$ which governs the time evolution

$$A(t) = e^{i\mathscr{L}t}A(0), \qquad i\mathscr{L}A = \frac{1}{i\hbar}[A, H], \tag{5}$$

is hermitian

$$\langle \mathscr{L}A, B\rangle = \langle A, \mathscr{L}B\rangle. \tag{6}$$

Let us consider a symmetry operation represented by an operator $\mathscr{U}$

$$\mathscr{U}H \equiv U^{+}HU = H.$$

With the use of the definition of $\mathscr{L}$ one obtains

$$\mathscr{U}\mathscr{L}A = U^{+}\mathscr{L}AU = \mathscr{L}U^{+}AU = \mathscr{L}\mathscr{U}A. \tag{7}$$

For $\mathscr{U}$ unitary the following relations hold

$$\langle \mathscr{U}A, \mathscr{U}B\rangle = \langle A, B\rangle, \quad \langle \mathscr{U}B\rangle_0 = \langle B\rangle_0. \tag{8a}$$

For an antiunitary operator $\mathscr{U}$ one gets (cf. Götze and Michel (1974))

$$\langle \mathscr{U}A, \mathscr{U}B\rangle = \langle A, B\rangle^{*}_{\overline{H}}, \quad \langle \mathscr{U}B\rangle_0 = \langle B\rangle_{0\overline{H}}, \tag{8b}$$

where the asterisk denotes a complex conjugation, and $\overline{H}$ is the time-reversed Hamiltonian.

Let us consider the dynamical part of the response function, connected with the Fourier transform of the time-dependent Kubo's correlator. The dynamical part of susceptibility reads

$$\beta G^{\text{isoth}}_{AB^{+}}(\omega) \equiv \lim_{\varepsilon\to 0^{+}} \operatorname{Lim} \frac{1}{N^2} \int\limits_{-\infty}^{0} dt e^{(\varepsilon - i\omega)t}\langle A, e^{i\mathscr{L}t}B\rangle. \tag{9}$$

Formally integrating one gets

$$\beta G^{\text{isoth}}_{AB^{+}}(\omega) = \lim_{\varepsilon\to 0^{+}} \operatorname{Lim} \frac{1}{N^2}(-i)\langle A, (-\omega + i\varepsilon - \mathscr{L})^{-1}B\rangle.$$

Introduce the resolvent operator

$$\mathscr{R}(z) \equiv (z - \mathscr{L})^{-1}, \tag{10}$$

where $z$ is a complex number. Hence one has

$$i\omega\beta G^{\text{isoth}}_{AB^{+}}(t) = \omega \lim_{\varepsilon\to 0^{+}} \operatorname{Lim} \frac{1}{N^2}\langle A, \mathscr{R}(-\omega + i\varepsilon)B\rangle. \tag{11}$$

Thus, the dynamical part of the response function $\beta G^{\text{isoth}}_{AB^{+}}(\omega)$ is a matrix element of the resolvent $\mathscr{R}(z)$ for $z = -\omega + i\varepsilon$. Let us consider the properties of the resolvent. The use of the definition (10) and the formula (5) yields

$$\mathscr{R}(z)B^{+} = -(\mathscr{R}(-z^{*})B)^{+}. \tag{12a}$$

Due to the hermicity of $\mathscr{L}$ one has

$$\langle A, \mathscr{R}(z)B\rangle = \langle \mathscr{R}(z^{*})A, B\rangle. \tag{12b}$$

Consider now the symmetry operations. For an unitary $\mathscr{U}$ commuting with the Liouvillean $\mathscr{L}$ one has

$$\langle \mathscr{U}A, \mathscr{R}(z)\mathscr{U}B\rangle = \langle A, \mathscr{R}(z)B\rangle. \tag{13a}$$

For an antiunitary symmetry operation $T$ with the representation $\mathscr{U}(T)$ one has for any $A$ and $B$

$$\langle \mathscr{U}A, \mathscr{R}(z^*)\mathscr{U}B\rangle = \langle A, \mathscr{R}(z)B\rangle_{\bar{H}}. \tag{13b}$$

The symmetry relations (8a, b), (13a, b) are very useful, as they reduce the number of independent elements of the susceptibility tensor.

### 3. *Response function of a ferroelectric of the order-disorder type to an external a.c. electric field*

Let us consider a ferroelectric with the Hamiltonian (cf. Blinc and Žekš (1972), Williams and Moore (1972)).

$$H = -\Gamma \sum_{l=1}^{N} S_l^x - \tfrac{1}{2} \sum_{l,m=1}^{N}{}' J(\boldsymbol{R}_l - \boldsymbol{R}_m) S_l^z S_m^z, \tag{14}$$

where $\Gamma > 0$. Since the pseudo-spin operators can be represented by Pauli matrices $\sigma^\alpha$

$$S_l^\alpha = \tfrac{1}{2}\sigma_l^\alpha \quad (\alpha = 1, 2, 3)$$

they obey the spin commutation rules

$$[S_l^\alpha, S_{l'}^\beta] = i \sum_{\gamma=1}^{3} \varepsilon_{\alpha\beta\gamma} S_l^\gamma \delta_{l,l'}. \tag{15}$$

The length of the polarization operator of the whole crystal is equal to

$$P = 2\mu \sum_{l=1}^{N} S_l^z,$$

where $\mu$ is the magnitude of the electric dipole moment of the ferroelectric two position dipole. This vector is parallel to the $c$-axis of the crystal.

In order to link the abstract pseudospin model to the real substance we ought to impose the symmetry properties of the real specimen on the Hamiltonian (14).

Let us begin with the time-reversal operation $T$. This is an antilinear symmetry operation. We ask for the representation $U(T)$ of $T$ for pseudospins $S_l^\alpha$. $U(T)$ is an antiunitary operator. Imposing three obvious physical requirements

$$\mathscr{U}(T)H \equiv U^+HU = H, \quad \mathscr{U}(T)P = P$$

and condition of preservation of the commutation rules (15), one finds

$$U(T) = K, \quad K^+ = K, \tag{16}$$

where the action of $K$ is simply to take the complex conjugate of any $c$-number. Since the only Pauli matrix with the complex elements is $\sigma^y$, one has

$$KS_l^yK = -S_l^y, \quad l = 1, \ldots, N.$$

Note that

$$K\mathscr{L}K = \mathscr{L}.$$

Next we consider the operations of the point symmetry group. The symmetry group of the paraelectric phase of the KDP crystals is $I\bar{4}2d(D_{2d}^{12})$. The symmetry of the ferroelectric phase is lower, since it belongs to the point group $mm2(C_{2v})$. Reasoning in the same manner as for the time-reversal operation one gets the pseudo-spin representation of the symmetry operations of KDP: (*i*) $1, S_4^2, \sigma_{v,x-y}, \sigma_{v,xy}$ corresponds to the unit matrix, (*ii*) $S_4, S_4^3, C_{2x}, C_{2y}$ have the representation

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{17}$$

Thus only $S^x$ does not change the spin under a transformation belonging to the second group[1].

The use of (17) and the independence of the trace on the choice of the basis yields for the paraelectric phase the exact relation

$$\chi_{zx} = \langle S^z, S^x \rangle = 0.$$

This is a well-known result usually derived with the help of equations of motion (cf. Pytte and Thomas (1968)). For the ferroelectric phase the operations of the second group are absent and $\chi_{zx}$ does not vanish.

Consider a linear change of the polarization $\langle P \rangle_0$, under the influence of the spatially unhomogeneous ac external field of the strength $E(x, t)$. The potential energy of the electric dipoles in this field is

$$H_1(t) = -\int_V d^3x P(x) E(x, t), \tag{18a}$$

where the operator of the polarization density is defined as

$$P(x) = \sum_{l=1}^{N} 2\mu S_l^z \delta(x - R_l) \equiv 2\mu S^z(x).$$

Introducing the Fourier transforms of the density of the $\alpha$-th component of the spin operator

$$S_k^\alpha \equiv \int_V d^3x e^{-ikx} S^\alpha(x),$$

the disturbance $H_1(t)$ (18) may be written as

$$H_1(t) = -\sum_k P_k^+ E_k(t). \tag{18b}$$

From (17) it follows that $K S_k^\alpha K = \varepsilon_\alpha S_{-k}^\alpha$, $\varepsilon_x = \varepsilon_z = 1$, $\varepsilon_y = -1$. Since we are interested in the linear change of the polarization $\langle P \rangle_0$, we obtain the polarization-polarization response function

$$\chi_{pp}(\omega, k) = \chi_{pp}(k) + \lim_{\varepsilon \to 0^+} \text{Lim}\, \omega N^{-2} \langle P_k, \mathcal{R}(-\omega + i\varepsilon) P_k \rangle. \tag{19}$$

[1] I am indebted to Dr J. Lorenc for the useful discussion of the symmetry properties of KDP.

Therefore, in order to find the response function for the considered system, one should study the matrix element of the resolvent $\mathscr{R}(z)$

$$\Phi_{pp}(z, k) = \langle P_k, \mathscr{R}(z)P_k\rangle = (2\mu)^2\langle S^z_k, \mathscr{R}(z)S^z_k\rangle.$$

Further we shall study the matrix element $\langle S^z_k, \mathscr{R}(z)S^z_k\rangle$. Actually, $\Phi_{pp}(z, k)$ is a matrix element of the matrix of the dynamical part of the response function.

Let us mention that due to experimentally observed critical slowing down of the polarization in the vicinity of the critical point, $P_k$ in this region is a slowly varying variable. Therefore one can use Kalashnikov's formula (2b). In order to get more information about the matrix of susceptibilities $\tilde{\chi}(\omega, k)$, let us consider the properties of the spin Hamiltonian with the transversal field term (14). The second order equation of motion for $P_k$ contains an oscillatory term.

In turn, $\Phi_{pp}(-\omega+i\varepsilon, k)$ contains an oscillating part. To select it from an incoherent fluctuating part, one has to consider additionally the matrix elements of $\mathscr{R}(z)$ between $S^y_k$ and mixed matrix elements.

Now, we will carry out this program. In our considerations we shall follow the paper by Götze and Michel (1974). We introduce the projector $\mathscr{P}$. For any variable $C$ one has

$$\mathscr{P}C = \sum_k \left\{ \frac{\langle C, S^z_k\rangle}{\langle S^z_k, S^z_k\rangle} S^z_k + \frac{\langle C, S^y_k\rangle}{\langle S^y_k, S^y_k\rangle} S^y_k \right\}. \tag{20a}$$

From this definition it follows that

$$\mathscr{P}^2 = \mathscr{P}.$$

The projector $\mathscr{P}$ is a hermitian operator. This follows from (3) and (20a)

$$\langle \mathscr{P}A, B\rangle = \langle A, \mathscr{P}B\rangle.$$

For any unitary or antiunitary symmetry operation $\mathscr{U}$ one has

$$\mathscr{U}\mathscr{P} = \mathscr{P}.$$

Since $S^z(x)$ is an even variable, and $S^y(x)$ is an odd variable under the time reversal, they are orthogonal, i.e.

$$\langle S^z(x), S^y(x')\rangle = 0, \tag{21a}$$

and from (21a) and the definition of the Fourier transform of $S^\alpha(x)$ it follows that $S^y_k, S^z_k$ are orthogonal, too

$$\langle S^z_k, S^y_{k'}\rangle = 0. \tag{21b}$$

Similarly

$$\langle S^z_k, S^x_{k'}\rangle = 0 \quad \text{for } T > T_c. \tag{22}$$

Below the temperature of the phase transition $T_c$, one can select the mean field term.

Similarly as in the case of the transversal field term this suggests that for the ordered phase one should enlarge the set of gross-variables and add $S^x_k$ to $\{S^z_k, S^y_k\}$. We stress that we shall not use the mean field approximation. Since $S_k^x$ is orthogonal to $S_k^y$ but not to $S_k^z$ one should introduce the new variable $X_k$, which is orthogonal to $S_k^z$

$$X_k = S_k^x - \frac{\langle S_k^x, S_k^z\rangle}{\langle S_k^z, S_k^z\rangle} S_k^z. \tag{23}$$

For the ordered phase the projector $\mathscr{P}$ projects in addition any variable $C$ on $X_k$

$$\mathscr{P}C = \sum_k \left\{ \frac{\langle C, S_k^z\rangle}{\langle S_k^z, S_k^z\rangle} S_k^z + \frac{\langle C, S_k^y\rangle}{\langle S_k^y, S_k^y\rangle} S_k^y + \frac{\langle C, X_k\rangle}{\langle X_k, X_k\rangle} X_k \right\}. \tag{20b}$$

In the present problem $\mathscr{P}$ is the projector on two or three dimensional subspace $\mathscr{H}_{\mathscr{P}} = \mathscr{P}\mathscr{H}$ spanned by $\{S_k^z, S_k^y\}$ or $\{S_k^z, S_k^y, X_k\}$, respectively. Let us denote the projector on the orthogonal complement $\mathscr{H}_{\mathscr{Q}} = \mathscr{H}\mathscr{Q}$ by $\mathscr{Q}$. The projectors $\mathscr{P}$ and $\mathscr{Q}$ fulfil the obvious relations

$$\mathscr{P}^2 = \mathscr{P} = \mathscr{P}^+, \quad \mathscr{Q}^2 = \mathscr{Q} = \mathscr{Q}^+, \quad \mathscr{Q}+\mathscr{P} = 1, \quad \mathscr{P}\mathscr{Q} = \mathscr{Q}\mathscr{P} = 0.$$

Using these formulas one can derive the following formal equation discussed in papers by Lanz and Lugiato (1969) and Götze and Michel (1974).

$$[z\mathscr{P} - \mathscr{P}\mathscr{L}\mathscr{P} - \mathscr{P}\mathscr{L}\mathscr{Q}\mathscr{R}_{\mathscr{Q}}(z)\mathscr{Q}\mathscr{L}\mathscr{P}]\mathscr{P}\mathscr{R}(z)\mathscr{P} = \mathscr{P}, \tag{24}$$

where

$$\mathscr{R}_{\mathscr{Q}}(z) = (z - \mathscr{L}_{\mathscr{Q}})^{-1},$$

and

$$\mathscr{L}_{\mathscr{Q}} = \mathscr{Q}\mathscr{L}\mathscr{Q}$$

is the reduction of $\mathscr{L}$ on the subspace $\mathscr{H}_{\mathscr{Q}}$. Introduce the matrix $\tilde{\Phi}(z, \boldsymbol{k})$ with the elements

$$\Phi_{\alpha\beta}(z, \boldsymbol{k}) = \langle A_k^\alpha, \mathscr{R}(z) A_k^\beta\rangle. \tag{25a}$$

For the paraelectric phase $(T > T_c)$ $A_k^1 = S_k^z$, $A_k^2 = S_k^y$. For the ferroelectric phase $(T < T_c)$ $A_k^1 = S_k^z$, $A_k^2 = S_k^y$, $A_k^3 = X_k$. The matrix $\tilde{\Phi}$ has the following property

$$\tilde{\Phi}^+(z, \boldsymbol{k}) = \tilde{\Phi}(z^*, \boldsymbol{k}). \tag{26a}$$

This follows from (4) and (12a, b). Using Eq. (24) one obtains for the matrix $\tilde{\Phi}(z, \boldsymbol{k})$ the representation derived by Götze and Michel (1974)

$$\Phi_{\alpha\gamma}(z, \boldsymbol{k}) = \sum_{\delta,\mu} \chi_{\alpha\delta}(\boldsymbol{k}) ([z^*\tilde{\chi}(\boldsymbol{k}) - \tilde{\omega}(\boldsymbol{k}) + \tilde{m}(z, \boldsymbol{k})]^{-1})_{\delta\mu} \chi_{\mu\gamma}(\boldsymbol{k}), \tag{27}$$

where $\tilde{\chi}(\boldsymbol{k})$ is a matrix with the elements $\langle A_k^\alpha, A_k^\gamma\rangle$. The matrix $\tilde{\omega}(\boldsymbol{k})$ is hermitian

$$\omega_{\alpha\beta}(\boldsymbol{k}) \equiv \langle A_k^\alpha, \mathscr{L} A_k^\beta\rangle = \omega_{\beta\alpha}^*(\boldsymbol{k}). \tag{28}$$

The last matrix $\tilde{m}(z, \boldsymbol{k})$ is defined in the subspace $\mathscr{H}_{\mathscr{Q}}$

$$m_{\alpha\beta}(z, \boldsymbol{k}) = -\langle \mathscr{Q}\mathscr{L}A_k^\alpha, \mathscr{R}_{\mathscr{Q}}(z)\mathscr{Q}\mathscr{L}A_k^\beta\rangle. \tag{25b}$$

Since is has the same structure as $\tilde{\Phi}(z, \boldsymbol{k})$ it fulfils

$$\tilde{m}^{+}(z, \boldsymbol{k}) = \tilde{m}(z^{*}, \boldsymbol{k}). \tag{26b}$$

Denote

$$\tilde{m}(\omega, \boldsymbol{k}) \equiv \lim_{\varepsilon \to 0^{+}} \mathrm{Lim}\, N^{-2}\tilde{m}(\omega + i\varepsilon, \boldsymbol{k}).$$

One has

$$\tilde{m}(\omega, \boldsymbol{k}) = \tilde{m}'(\omega, \boldsymbol{k}) - i\tilde{m}''(\omega, \boldsymbol{k}), \tag{28a}$$

where from (26b) and (28a)

$$m''^{*}_{\alpha\beta}(\omega, \boldsymbol{k}) = m''_{\beta\alpha}(\omega, \boldsymbol{k}), \qquad m'^{*}_{\alpha\beta}(\omega, \boldsymbol{k}) = m'_{\beta\alpha}(\omega, \boldsymbol{k}). \tag{28b, c}$$

The matrix $\tilde{m}''(\omega, \boldsymbol{k})$ is positive.

From the definition (25a) and (4) it follows that

$$\Phi^{*}_{\alpha\beta}(z, \boldsymbol{k}) = -\Phi_{\alpha\beta}(-z^{*}, -\boldsymbol{k})$$

and similarly from (25b)

$$m^{*}_{\alpha\beta}(z, \boldsymbol{k}) = -m_{\alpha\beta}(-z^{*}, -\boldsymbol{k}). \tag{29}$$

Using the identity

$$\langle \mathscr{L}A, B\rangle = \frac{1}{\hbar}\langle [B^{+}, A]\rangle_{0},$$

one obtains the $\tilde{\omega}(\boldsymbol{k})$ matrix.

As usually, that matrix of restoring forces $\tilde{\Omega}(\boldsymbol{k})$ is defined as

$$\Omega(\boldsymbol{k}) \equiv (\mathrm{Lim}\, N^{-2}\tilde{\omega}(\boldsymbol{k}))\tilde{\chi}^{-1}(\boldsymbol{k}).$$

For the ferroelectric phase one has

$$\tilde{\Omega}(\boldsymbol{k}) = \begin{bmatrix} 0 & i\Omega_{1} & 0 \\ -i\Omega_{1}\dfrac{\chi_{y}}{\chi_{11}(\boldsymbol{k})} & 0 & i\Omega_{2}(\boldsymbol{k}) \\ 0 & -i\Omega_{2}^{*}(\boldsymbol{k})\dfrac{\chi_{33}(\boldsymbol{k})}{\chi_{y}} & 0 \end{bmatrix}, \tag{30}$$

where

$$\Omega_{1} = \Gamma/\hbar, \quad \Omega_{2}(\boldsymbol{k}) = (\hbar\chi_{33}(\boldsymbol{k}))^{-1}\left(N^{-1}\langle S_{0}^{z}\rangle_{0} + \frac{\chi_{zx}(\boldsymbol{k})\chi_{y}}{\chi_{11}(\boldsymbol{k})}\Gamma\right),$$

$$\langle S_{0}^{\alpha}\rangle_{0} = \langle S_{k=0}^{\alpha}\rangle \equiv \langle S_{\alpha}\rangle_{0}, \quad (\alpha = x, y, z),$$

$$\chi^{*}_{zx}(\boldsymbol{k}) = \chi_{zx}(-\boldsymbol{k})$$

hence $\chi_{zx}(\boldsymbol{k})$ is real for $|\boldsymbol{k}| = 0$.

In derivation of Eq. (30) we accounted for an exact relation

$$\langle S^y_k, S^y_k\rangle = \frac{\langle S^x_0\rangle_0}{\Gamma}.$$

Pytte and Thomas (1968) have found the critical behaviour of susceptibilities in the mean field approximation. The polarization-polarization susceptibility is divergent in both phases, $\chi_{zx}$ is divergent in the ferroelectric phase only. The susceptibilities $\chi_{yy} \equiv \chi_y, \chi_{xx}$ are regular in the whole temperature range. Since

$$\mathrm{Lim}\,(N^{-2}\langle X_k, X_k\rangle) = \mathrm{Lim}\,(N^{-2}\langle S^x_k, S^x_k\rangle) - \mathrm{Lim}\,(N^{-2}|\langle S^z_k, S^x_k\rangle|^2\langle S^z_k, S^z_k\rangle) \qquad (31)$$

the susceptibility $\chi_{33}$ is regular, too.

For the paraelectric phase the matrix of restoring forces $\tilde{\Omega}(k)$ is much simpler

$$\tilde{\Omega}(k) = \begin{bmatrix} 0 & i\Omega_1 \\ -i\Omega_1\chi_y\chi_{11}^{-1}(k) & 0 \end{bmatrix}. \qquad (32)$$

Consider the characteristic frequencies. For the ferroelectric phase, one of them equals zero

$$\lambda_1 = 0,$$

and two others $\lambda_2, \lambda_3$ are equal

$$\lambda_{2,3}(k) = \pm[\Omega_1^2\chi_y\chi_{11}(k) + |\Omega_2(k)|^2\chi_{33}(k)\chi_y^{-1}]. \qquad (33a)$$

The eigenfrequencies $\lambda_2, \lambda_3$ are soft. This is due to

$$\langle S^z_k\rangle_0 \to 0 \text{ and } \chi_{11}(k) \to \infty \text{ for } |k| \to 0 \text{ and } T \to T_c.$$

In the spin space the motion corresponding to the eigenvalue $\lambda_1 = 0$ occur in the plane perpendicular to $A^2_k$. The eigenfrequencies for the paraelectric phase are soft too

$$\lambda^2(k) = \Omega_1^2\chi_y\chi_{11}^{-1}(k), \qquad (33b)$$

hence, for small $|k|$ from the results of Patte and Thomas (1968) it follows that

$$\lambda^2(k) \simeq \Omega_1^2\Gamma^{-1}\,\mathrm{Lim}\left(\frac{\langle S^x_0\rangle_0}{N}\right)[ak^2 + b_+(T-T_c)] \quad \text{for } T \to T_c^+.$$

The resolvent $\tilde{m}(z, k)$ is the mass operator for the pseudospin waves. It is a quantity of the same type as $\tilde{\Phi}(z, k)$ but defined in the subspace $\mathscr{H}_{\mathscr{Q}}$. If this subspace contains only quickly changing variables, one can expect that $\tilde{m}(\omega, k)$ is an analytic function of $|k|$ and $\omega$. In such a case it is a good candidate for approximations. If $\mathscr{H}_{\mathscr{Q}}$ contains another slowly varying variable (e.g. energy density) one should further enlarge the set of variables.

Consider the "mass operator" $\tilde{m}(z, k)$ for a simpler case of the paraelectric phase. Since $\mathscr{Q}\mathscr{L}S^z_k = 0$ the $\tilde{m}(z, k)$ matrix has only one nonvanishing element $\tilde{m}_{22}(z, k)$. The use of Eq. (19) and the thermodynamical limit of (27) yieds

$$\chi_{pp}(\omega, k) = \frac{-(2\mu)^2\chi_y\Omega_1^2}{\omega^2 - \dfrac{m_{22}(-\omega+i\varepsilon, k)}{\chi_y}\,\omega - \dfrac{\chi_y}{\chi_{11}(k)}\,\Omega_1^2}. \qquad (34a)$$

Since $m'_{22}(\omega, \boldsymbol{k})$ is an odd function of the frequency $\omega$ and $m''_{22}(\omega, \boldsymbol{k})$ is an even function of frequency, and both are even functions of the wave vector $\boldsymbol{k}$ (cf. (35b, c, d)) our formula gives for small $\omega$ the generalization of the phenomenological formula derived by Blinc and Žekš (1972). Let us mention that their formulas correspond to our $\chi_{pp}(-\omega, \boldsymbol{k})$. A generalization consists in the renormalization effects — the change of the height of the peak of the absorptive part of the susceptibility and the shift of eigenfrequencies.

From the formula (34a) it follows that in the paraelectric phase there exist two overdamped soft modes. Since the projection method yields a formula for damping in the form of the Fourier transform of the time and space dependent correlation function, that shows advantages of the projection method. Contrary to the phenomenological formula, this correlation function can be studied further. For example, one can use the mode-mode coupling approximation.

In particular we expect that such calculations could discriminate between existing models of KDP.

To show the power of the method let us consider the coupling to the heat conduction in the paraelectric phase. Introduce the energy density

$$H(\boldsymbol{x}) = -\Gamma S^x(\boldsymbol{x}) - \tfrac{1}{2}\int_V d^3y J(\boldsymbol{x}-\boldsymbol{y}) S^z(\boldsymbol{x}) S^z(\boldsymbol{y}).$$

The Fourier transform reads

$$H_{\boldsymbol{k}} = -\Gamma S^x_{\boldsymbol{k}} - \frac{1}{2V}\sum_{\boldsymbol{k}'} J(\boldsymbol{k}') S^z_{\boldsymbol{k}} S^z_{\boldsymbol{k}-\boldsymbol{k}'}.$$

Let $\mathscr{P}_H$ be the projector on $H_{\boldsymbol{k}}$

$$\mathscr{P}_H A = \sum_{\boldsymbol{k}} \langle A, H_{\boldsymbol{k}} \rangle \langle H_{\boldsymbol{k}}, H_{\boldsymbol{k}} \rangle^{-1} H_{\boldsymbol{k}},$$

$\mathscr{Q}_H = 1 - \mathscr{P}_H$ projects on the orthogonal complement $\mathscr{H}_{\mathscr{Q}H}$. One can write

$$m_{22}(z, \boldsymbol{k}) = -\langle (\mathscr{P}_H + \mathscr{Q}_H) \mathscr{Q} \mathscr{L} S^y_{\boldsymbol{k}}, \mathscr{R}_{\mathscr{Q}}(z) (\mathscr{P}_H + \mathscr{Q}_H) \mathscr{Q} \mathscr{L} S^y_{\boldsymbol{k}} \rangle.$$

Since $S^y_{\boldsymbol{k}}$ is odd and $H_{\boldsymbol{k}}$ is even variable under the time reversal $T$, the only nonvanishing element of $m_{22}$ is

$$m_{22}(z, \boldsymbol{k}) = -\langle \mathscr{Q}_H \mathscr{Q} \mathscr{L} S^y_{\boldsymbol{k}}, \mathscr{R}_{\mathscr{Q}}(z) \mathscr{Q}_H \mathscr{Q} \mathscr{L} S^y_{\boldsymbol{k}} \rangle.$$

This means that $m_{22}(z, \boldsymbol{k})$ does not exhibit the diffusion pole. In the paraelectric phase and in linear approximation the heat diffusion does not influence the polarization. This shows that the central peak discovered in the paraelectric phase has different origin than the coupling to the heat conductivity.

Consider the matrix $\tilde{m}(z, \boldsymbol{k})$ for the ferroelectric phase. All matrix elements $m_{1\alpha}(z, \boldsymbol{k}), m_{\alpha 1}(z, \boldsymbol{k})$ $(\alpha = 1, 2, 3)$ are equal zero. Now we will study the symmetry properties of the nonvanishing elements. Using (26b), (29) and (13b), which for our case reads

$$m^*_{\alpha\beta}(z^*, \boldsymbol{k}) = \varepsilon_\alpha \varepsilon_\beta m_{\alpha\beta}(z, -\boldsymbol{k}),$$

and also (28a) for the case $z = \omega + i\varepsilon$, we obtain the set of equations connecting non-vanishing matrix elements. The diagonal matrix elements are real

$$m'^{*}_{\alpha\alpha}(\omega, \boldsymbol{k}) = m'_{\alpha\alpha}(\omega, \boldsymbol{k}),$$

$$m''^{*}_{\alpha\alpha}(\omega, \boldsymbol{k}) = m''_{\alpha\alpha}(\omega, \boldsymbol{k}). \tag{35a}$$

For $\omega \to 0$ the only nonvanishing diagonal matrix element is $m''_{\alpha\alpha}$. This follows from

$$m'_{\alpha\alpha}(-\omega, \boldsymbol{k}) = -m'_{\alpha\alpha}(\omega, \boldsymbol{k}), \tag{35b}$$

$$m''_{\alpha\alpha}(-\omega, \boldsymbol{k}) = m''_{\alpha\alpha}(\omega, \boldsymbol{k}). \tag{35c}$$

Besides, the diagonal elements are even functions of $\boldsymbol{k}$

$$m'_{\alpha\alpha}(\omega, -\boldsymbol{k}) = m'_{\alpha\alpha}(\omega, \boldsymbol{k}), \quad m''_{\alpha\alpha}(\omega, -\boldsymbol{k}) = m''_{\alpha\alpha}(\omega, \boldsymbol{k}). \tag{35d}$$

For off-diagonal elements relations (35b, c) have opposite signs

$$m'_{23}(-\omega, \boldsymbol{k}) = m'_{23}(\omega, \boldsymbol{k}), \quad m''_{23}(-\omega, \boldsymbol{k}) = -m''_{23}(\omega, \boldsymbol{k}). \tag{35e}$$

The matrix elements $m'_{23}$, $m''_{23}$ obey additionally two conditions

$$m'^{*}_{23}(\omega, \boldsymbol{k}) = m'_{32}(\omega, \boldsymbol{k}), \quad m''^{*}_{23}(\omega, \boldsymbol{k}) = -m''_{32}(\omega, \boldsymbol{k}), \tag{35f}$$

$$m'_{23}(\omega, -\boldsymbol{k}) = -m'_{32}(\omega, \boldsymbol{k}), \quad m''_{23}(\omega, -\boldsymbol{k}) = -m''_{32}(\omega, \boldsymbol{k}). \tag{35g}$$

Hence, for $|\boldsymbol{k}| = 0$, $m'_{23}$ is purely imaginary: $m'_{23}(\omega) = i\gamma(\omega)$. From Jacobi's criterion of positiveness of a hermitian matrix it follows that in the case of the paraelectric phase $m''_{22}(\omega, \boldsymbol{k}) > 0$.

For the ferroelectric phase, $m''_{22}(\omega, \boldsymbol{k}) + m''_{33}(\omega, \boldsymbol{k}) > 0$ and $m''_{22}(\omega, \boldsymbol{k}) m''_{33}(\omega, \boldsymbol{k}) - |m''_{23}(\omega, \boldsymbol{k})|^2 > 0$, therefore for $|\boldsymbol{k}| \to 0$ we get weaker conditions

$$m''_{22}(\omega) > 0, \quad m''_{33}(\omega) > 0.$$

In the same manner as for the paraelectric phase, we find the response function

$$\chi_{pp}(\omega, k) = \frac{(2\mu)^2}{\chi_y} \times \frac{\omega_1^2\left(-\omega + \dfrac{m_{33}}{\chi_{33}}\right)}{\omega\left(\omega - \dfrac{m_{22}}{\chi_y}\right)\left(\omega - \dfrac{m_{33}}{\chi_{33}}\right) - \dfrac{|i\omega_2 + m_{23}|^2}{\chi_{33}\chi_y}\,\omega - \dfrac{\omega_1^2}{\chi_{11}\chi_y}\left(\omega - \dfrac{m_{33}}{\chi_{33}}\right)}, \tag{34b}$$

where

$$\omega_1 = (N\hbar)^{-1}\langle S_0^x\rangle_0, \quad \omega_2(k) = \hbar^{-1}\left(N^{-1}\langle S_0^z\rangle_0 + \frac{\chi_{zx}(k)}{\chi_{zz}(k)N}\langle S_0^x\rangle_0\right).$$

Since the formula (34a) is rather complicated, we have dropped the arguments of the correlators. They are $(-\omega)$ and $\boldsymbol{k}$. From this formula it follows that $m_{23}$ renormalizes the frequency $\omega_2$, for small $\omega$ and $|k| \to 0$. Besides, the real parts of $m_{\alpha\alpha}$ and imaginary one of $m_{23}$ change the height of the peak of the adsorptive part of susceptibility $\chi_{pp}(\omega)$. Since the relaxation times $T_1$, $T_2$ connected with the imaginary parts of $m_{22}$, $m_{33}$, respectively, are in the simplest approximation the adjustable parameters, we can absorb any renormalization factors into their definitions.

### 4. *Bloch equations describing a ferroelectric of the order-disorder type*

It is well-known that having the response function one can derive from it the Generalized Bloch equations. In the frame of Kubo's method the general derivation was given by Götze and Michel (1974). Since the Bloch equations form the basis for the description of various experiments, we shall derive them for a ferroelectric of the order-disorder type.

Let us consider a slightly more general case of several external fields $\mathscr{F}_\gamma(t)$ ($\gamma = 1, 2, \ldots s$). In such a case

$$H_1(t) = -\sum_{\gamma=1}^{s} B_\gamma^+ \mathscr{F}_\gamma(t).$$

This disturbance changes the equilibrium mean values of the variables $A_\alpha$ ($\alpha = 1, \ldots, n$). In the linear approximation in the strengths $\mathscr{F}_\gamma$, the Fourier transform of these changes are equal (cf. (2a))

$$\lim N^{-1}\Delta\langle A_\alpha\rangle(\omega) = \sum_{\gamma,\delta,\mu} \chi_{\alpha\gamma}(-\omega)(\tilde{\chi}^{-1})_{\gamma\delta}\chi_{\delta\mu}\mathscr{F}_\mu(\omega), \tag{2a}$$

where

$$\chi_{\alpha\gamma}(\omega) = \chi'_{\alpha\gamma} + \lim_{\varepsilon\to 0^+} \operatorname{Lim} N^{-2}\omega\Phi_{\alpha\gamma}(-\omega+i\varepsilon).$$

Let us introduce the Fourier transform of the memory kernel

$$\tilde{M}(\omega) = \tilde{m}(\omega)\tilde{\chi}^{-1}.$$

Using the formula (27) in the thermodynamic limit, one can write $\tilde{\chi}(\omega)\tilde{\chi}^{-1}$ as

$$\tilde{\chi}(\omega)\tilde{\chi}^{-1} = [-\omega\tilde{1}-\tilde{\Omega}+\tilde{M}(-\omega)]^{-1}[-\tilde{\Omega}+\tilde{M}(-\omega)].$$

Now (2a) can be rewritten in the following form

$$\omega \operatorname{Lim} N^{-1}\Delta\langle\tilde{A}\rangle(\omega) = \tilde{\Omega}\delta\langle\tilde{A}\rangle(\omega) - \tilde{M}(\omega)\delta\langle\tilde{A}\rangle(\omega), \tag{36}$$

where $\delta\langle\tilde{A}\rangle(\omega)$ is a column matrix with the $\alpha$-th element equal to

$$\delta\langle A_\alpha\rangle(\omega) = \operatorname{Lim} N^{-1}\Delta\langle A_\alpha\rangle(\omega) - \sum_\gamma \chi_{\alpha\gamma}\mathscr{F}_\gamma(\omega).$$

The Fourier transform of Eq. (36) gives the Generalized Bloch Equation with an allowance of the memory effects. The discussion of these equations can be found, for example, in the paper by Götze and Michel (1974). Generally $\Delta\langle A_\alpha\rangle(t)$ relaxes to some local-equilibrium value, which depends on the initial conditions imposed on Liouville's equation.

Let us return to our special case of a hydrogen-bonded ferroelectric. The paraelectric phase is described with the help of two Bloch-like equations. In the case of a disturbance homogeneous in space $|\boldsymbol{k}| = 0$ one obtains for the Fourier transform of Eq. (36)

$$\frac{d}{dt}\langle P_0\rangle(t) = -\Omega_1 2\mu\langle S_0^y\rangle(t), \tag{37a}$$

$$\frac{d}{dt}2\mu\langle S_0^y\rangle(t) = -\frac{1}{T_2}2\mu\langle S_0^y\rangle(t)+\Omega_1\frac{\chi_y}{\chi_{11}}\Delta\langle P_0\rangle(t)-(2\mu)^2\Omega_1\chi_y E(t). \tag{37b}$$

For simplicity in these equations we have neglected all renormalization effects connected with the higher order terms of the Taylor expansion of $M_{22}(\omega)$ in $\omega$, i.e. we have taken

$$\lim_{\omega\to 0} M_{22}(\omega) = -iT_2^{-1}, \quad (T_2 > 0).$$

In a similar approximation, the set of equations for the ferroelectric phase reads

$$\frac{d}{dt}\langle P_0\rangle(t) = -\Omega_1 2\mu\langle S_0^y\rangle(t), \tag{38a}$$

$$\frac{d}{dt}2\mu\langle S_0^y\rangle(t) = \left[\Omega_1\frac{\chi_y}{\chi_{11}}+\frac{\chi_{zx}}{\chi_{11}}\Omega_2'\right]\Delta\langle P_0\rangle(t)-\frac{1}{T_2}2\mu\langle S_0^y\rangle(t)$$
$$-\Omega_2' 2\mu\langle S_0^x\rangle(t)-(2\mu)^2\Omega_1\chi_y E(t), \tag{38b}$$

$$\frac{d}{dt}2\mu\langle S_0^x\rangle(t) = \frac{\chi_{zx}}{\chi_{11}T_1}\Delta\langle P_0\rangle(t)-\left[\Omega_1\frac{\chi_{zx}}{\chi_{11}}-\Omega_2'\frac{\chi_{33}}{\chi_y}\right]2\mu\langle S_0^y\rangle(t)$$
$$-\frac{1}{T_1}2\mu\Delta\langle S_0^x\rangle(t), \tag{38c}$$

where in the lowest approximation

$$\lim_{\omega\to 0} M_{33}(\omega) = -iT_1^{-1}, \quad (T_1 > 0)$$

$$\lim_{\omega\to 0} m_{23}(\omega)/\chi_{33} = i\gamma,$$

and

$$\Omega_2' = (\Omega_2-\gamma).$$

Both sets are different from the well-known set of Bloch equations for a paramagnet. The difference is due to both the high anisotropy and low symmetry of the considered system.

Our sets are different also from those derived by Blinc and Žekš (1972). They start with the set of equations for less pathological system and then tried to lower the symmetries of this set. Since $S_0^x$ is not a thermodynamic variable in the paraelectric phase, there are only two equations for the paraelectric phase. In spite of this difference, for the paraelectric phase and for small wave-vectors and frequencies, the response function in both approaches is the same. This is due to the fact that for a paramagnet the equations for the transversal components are decoupled from the equations for longitudinal one. The sets (37) and (38) should be used for description of various experiments which can be carried out on the hydrogen bonded ferroelectrics.

## 5. *Summary and final remarks*

Let us summarize our results. The critical slowing down of the polarization indicates that in the vinicity of phase transition $P$ is the thermodynamic variable. In order to separate the systematic oscillations from uncoherent fluctuations we should additionally use other pseudo-spin components.

Of course, this is the simplest choice of the set of thermodynamic variables describing the dynamics of critical fluctuations, valid in the so called classical region of the phase transition. In the paraelectric phase, the limit from above corresponds to the region, where the critical slowing down is fully developed, the lower limit can be obtained from Ginzburg criterion. This criterion gives also the upper limit for the ferroelectric phase. In the really critical region the linear response approximation is not valid. Since we are looking for the response of thermodynamic variable under influence of the field coupled to the same thermodynamic variable, we can use the Kalashnikov theory (1974). Hence, our response functions have the correct static limit. The study of the laws of transformation of the components of pseudospin operators under the symmetry operations considerably simplifies the response functions. In particular, we have shown exactly that in the paraelectric phase an unhomogeneous electric field does not induce the heat flow. Since in the discussed temperature regions the mass operators are defined in the subspace of the Hilbert space of variables $\mathscr{H}_{\mathscr{D}}$, we can treat them as regular function of $\omega$ and $\boldsymbol{k}$. In this manner we can introduce the relaxation times $T_1$, $T_2$ and the frequency shift.

They are given in the form of correlation functions, and could be studied further. This possibility is very interesting for the paraelectric phase, since one can use the mode-mode coupling with really few variables. The comparison of the result of calculations with experimental results could discriminate between various models of the critical dynamics of KDP (Blinc and Žekš (1972); Cowley and Coombs (1973)).

For the ferroelectric phase one should study the pseudospin waves.

From the response functions we derived two sets of Bloch-like equations. For simplicity, we considered only the case of an homogeneous electric field. Then, one can drop the density of energy, and we deal in the ferroelectric case, with the set of three equations only. Our equations are not more complicated than these given by Blinc and Žekš (1972). The equations for paraelectric phase are so simple, that it is possible to solve them in quadratures. Hence, one can study the possibility of various experiments.

The Fourier transforms of sesceptibilities correspond to the continuous waves method. It is well known that such a Fourier analysis can be done with the help of a single experiment with pulses of field. Thus, one can study the "free induction" experiments, or experiments with several pulses of the electric field. This last type of experiments could be interesting, since they could give the "pseudospin echoes".

But since the direction of polarization is fixed, this possibility is hypothetical one. However, in fact some experiments with the sequence of pulses of microwaves were performed by Frenois et al. (1976). They attribute the existence of echoes to the deformation field of the lattice (piezoelectric coupling).

We hope to return to these problems in future.

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Note added in proof:

The symmetry propertes (18) follow also from the genernl invariance of the Hamiltonian (14) under the $\pi$-rotation in the spin space about the $x$ axis

$$e^{i\pi S_0^x} H e^{-i\pi S_0^x} = H,$$

hence the operator $\prod_{i=1}^{N} S_i^x$ is the constants of motion. This rotation changes the sign of $S_i^z$ and $S_i^y$ but not $S_i^x$. The average $\langle S_z \rangle_0$ for $T < T_c$ should be understood as the quasi-average. The formula (34a) suplemented by the terms connected with the coupling to the optical mode does fit the experimental data of Lagakos and Cummins (*Phys. Rev.* **B10**, 1063 (1974)) much better than the expression derived by Blinc and Žekš (E. Courtens, private information).

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