PROPERTIES OF SOLUTIONS OF BLOCH-TYPE EQUATIONS FOR THE PARAELECTRIC PHASE OF KDP

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(Received December 11, 1978)

Exact solutions for two sets of Bloch-like equations describing the paraelectric phase of the model of KDP were studied. The general properties of both solutions are the same. However, in numerical calculations they differ significantly. A modification of the decay law connected with the soft mode frequency fluctuations is considered.

A critical behaviour of the model of hydrogen bonded ferroelectric is described by the Bloch-type equations. In the literature two such sets are known. One was derived within the frame of the mean field theory (MFA) [1], the other was obtained by using the Mori's method [2]. It is the purpose of this note to compare the solutions of both sets. We shall consider only the paraelectric phase for which it is easy to find exact solutions.

Both sets of equations describe the motion of the Fourier transform of deviations of pseudospin components $\delta\langle S_k^\alpha\rangle_t$. These deviations are induced by an external electric field E_t. For simplicity we shall consider the homogeneous case ($k = 0$).

These equations are [2]

$$\frac{d}{dt}\delta\langle S_0^y\rangle_t = -\frac{1}{T_2}\delta\langle S_0^y\rangle_t + \frac{\Omega^2}{\Omega_1}\delta\langle S_0^z\rangle_t - 2\mu E_t\langle S_0^x\rangle, \tag{1a}$$

$$\frac{d}{dt}\delta\langle S_0^z\rangle_t = -\Omega_1\delta\langle S_0^y\rangle_t, \tag{1b}$$

and describe the mode which becomes soft, i.e., the oscillations frequency Ω diminishes when the temperature nears the critical temperature. The tunneling frequency is equal

* Work supported by the US National Science Foundation under Grant GF-41959 from the Joint Research Program in Theoretical Physics between the State University of New York at Stony Brook and the Wrocław University.

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to Ω_1, 2μ is the dipole moment of two-state dipole and $\langle S_0^x \rangle$ is the mean value of the x component of the total pseudospin. Finally, T_2 is the relaxation time.

In order to obtain the set of equations in MFA one should replace the soft mode frequency by its mean field value Ω_{MFA} and add two terms to the second equation:

$$\frac{d}{dt}\delta\langle S_0^y\rangle_t = -\frac{1}{T_2}\delta\langle S_0^y\rangle_t + \frac{\Omega_{\text{MFA}}^2}{\Omega_1}\delta\langle S_0^z\rangle_t - 2\mu E_t\langle S_0^x\rangle, \tag{2a}$$

$$\frac{d}{dt}\delta\langle S_0^z\rangle_t = -\Omega_1\delta\langle S_0^y\rangle_t - \frac{\Omega_{\text{MFA}}}{T_2\Omega_1^2}\delta\langle S_0^z\rangle_t + \frac{2\mu E_t\langle S_0^x\rangle}{\Omega_1 T_2}. \tag{2b}$$

Stationary solutions of both equations are similar. Namely, $\delta\langle S_0^y\rangle_{\text{St}} = 0$ in both cases and $\delta\langle S_0^z\rangle_{\text{St}} = 2\mu\chi_{zz}E$. In the case of MFA one should replace the exact value of the isothermal susceptibility χ_{zz} by the χ_{zz}^{MFA}.

Both equations are correct. The first one indicates that in the stationary regime the current through the barriers vanishes. It is easy to find the formal solution for both sets of equations. They have the following form

$$\begin{pmatrix} P \\ J \end{pmatrix}(t) = \hat{R}(t-t_0)\begin{pmatrix} P_0 \\ J_0 \end{pmatrix} + \begin{pmatrix} \Delta P \\ \Delta J \end{pmatrix}(t, t_0, E), \tag{3}$$

where we have introduced the polarization

$$P(t) = 2\mu\delta\langle S_0^z\rangle_t$$

and "current"

$$J(t) = 2\mu\delta\langle S_0^y\rangle_t.$$

The evolution matrix $\hat{R}$ contains both the "rotation" and the decay. For the first set we obtain

$$\hat{R}(t-t_0) = (\lambda_1-\lambda_2)^{-1}\begin{pmatrix} \lambda_1 e^{\lambda_2(t-t_0)} - \lambda_2 e^{\lambda_1(t-t_0)}; & -\Omega_1(e^{\lambda_1(t-t_0)} - e^{\lambda_2(t-t_0)}) \\ \lambda_1\lambda_2(e^{\lambda_1(t-t_0)} - e^{\lambda_2(t-t_0)}); & \lambda_1 e^{\lambda_1(t-t_0)} - \lambda_2 e^{\lambda_2(t-t_0)} \end{pmatrix},$$

where

$$\lambda_{1,2} = \tfrac{1}{2}(-T_2^{-1} \pm \sqrt{T_2^{-2} - 4\Omega^2}).$$

For the second set the evolution matrix is

$$R(t-t_0) = (\lambda_1'-\lambda_2')^{-1}\begin{pmatrix} \left(\lambda_2' + \frac{1}{T_2}\right)e^{\lambda_2'(t-t_0)} - \left(\lambda_1' + \frac{1}{T_2}\right)e^{\lambda_1'(t-t_0)}; & \Omega_1(e^{\lambda_1'(t-t_0)} - e^{\lambda_2'(t-t_0)}) \\ (e^{\lambda_2'(t-t_0)} - e^{\lambda_1'(t-t_0)})\dfrac{\Omega_{\text{MFA}}^2}{\Omega_1}; & \left(\lambda_2' + \frac{1}{T_2}\right)e^{\lambda_1'(t-t_0)} - \left(\lambda_1' + \frac{1}{T_2}\right)e^{\lambda_2'(t-t_0)} \end{pmatrix},$$

where

$$\lambda'_{1,2} = -\gamma \pm (\gamma^2 - \overline{\Omega}^2_{\mathrm{MFA}})^{1/2},$$

$$\gamma = \frac{1}{2T_2}\left(1+\frac{\Omega^2_{\mathrm{MFA}}}{\Omega_1^2}\right), \quad \overline{\Omega}^2_{\mathrm{MFA}} = \frac{T_2\Omega_1^2+1}{T_2^2\Omega_1^2}\,\Omega^2_{\mathrm{MFA}}.$$

The second term of Eq (3) describes the change of the polarization and current under the influence of an a.c. electric field. For set (1) this change is equal to

$$\begin{pmatrix} \Delta P \\ \Delta J \end{pmatrix}(t, t_0, E) = \frac{\Omega_1 2\mu\langle S_0^x\rangle}{\lambda_1-\lambda_2}\begin{pmatrix} \int_{t_0}^{t} d\tau E(\tau)\,(e^{\lambda_1(t-\tau)}-e^{\lambda_2(t-\tau)}) \\ -\Omega_1^{-1}\int_{t_0}^{t} d\tau E(\tau)\,(\lambda_1 e^{\lambda_1(t-\tau)}-\lambda_2 e^{\lambda_2(t-\tau)}) \end{pmatrix}.$$

The corresponding equations for the second set are more complicated

$$\begin{pmatrix} \Delta P \\ \Delta J \end{pmatrix}(t, t_0; E) = \frac{\Omega_1 2\mu\langle S_0^x\rangle}{\lambda'_2-\lambda'_1}$$

$$\times \begin{bmatrix} \int_{t_0}^{t} d\tau E(\tau)\left\{\left(1+\frac{\lambda'_2+T_2^{-1}}{\Omega_1^2 T_2}\right)e^{\lambda_2'(t-\tau)}-\left(1+\frac{\lambda'_1+T_2^{-1}}{\Omega_1^2 T_2}\right)e^{\lambda_1'(t-\tau)}\right\} \\ -\frac{1}{\Omega_1}\int_{t_0}^{t} d\tau E(\tau)\,\{(\lambda'_1+2\gamma)e^{\lambda_2'(t-\tau)}-(\lambda'_2+2\gamma)e^{\lambda_1'(t-\tau)}\} \end{bmatrix}.$$

As the phase transition temperature is approached λ_1 and λ'_1 vanish; $\lambda_2, \lambda'_2 \to -\frac{1}{T_2}$ and $\gamma \to \frac{1}{2T_2}$. Within this limit solutions for $\delta\langle S_0^y\rangle_t$ are identical and apart from nonessential changes, the solutions for $\delta\langle S_0^z\rangle_t$ differ by the term proportional to $\Omega_1 T_2$.

Next we shall examine the saturation case where $E_t = \mathrm{const}$ and $t \to \infty$. We obtain solutions which coincide with the stationary ones:

$$\delta\langle S_0^y\rangle_\infty = 0, \quad \delta\langle S_0^z\rangle_\infty = 2\mu\chi_{zz}E.$$

Opposite to the set of Bloch equations for a paramagnet [3], sets (1) and (2) do not contain the phase memory. Thus, the pseudospin echo is excluded. Only the analog of the free induction is present that is, the free decay of the induced polarization.

One cannot exclude the pseudospin echo for the ferroelectric phase, because in such a case, one deals with a set of three more complicated equations.

We see that the behaviour of both solutions in all examined cases is quite similar. Nevertheless, they are not identical. In fact, Courtens [4] considered the model of pseudospins coupled to the optical phonons. He found that the fit of the Raman data of Lakagos and Cummins [5] with the susceptibility following from the MFA set od equations improves when the tunneling frequency diminishes. For our set of equations the fit is stable and $\hbar\Omega_1$ is $\sim 112\ \text{cm}^{-1}$, and $T_2 \sim 176\ \text{cm}^{-1}$ [4]. The usual choice corresponds to one half of our tunneling frequency.

The last problem which we shall consider is the modification of the decay law by the fluctuations of the soft mode frequency.

Suppose that $\xi^{-1} = \Omega T_2 \gg 1$ and that the soft mode frequency fluctuates with the Gaussian distribution function

$$g(\Delta\Omega) = 2\pi(\langle(\Delta\Omega)^2\rangle)^{-1/2} \exp\left\{-\frac{(\Delta\Omega)^2}{\langle(\Delta\Omega)^2\rangle}\right\}. \qquad (4)$$

Further we shall consider the evolution matrix in the approximation linear in ξ. Taking into account the fluctuations $\Omega \to \Omega+\Delta\Omega$ and averaging the evolution matrix over the distribution (4), we find that the resulting evolution matrix contains the following factor

$$\exp\left\{-\frac{1}{2T_2}(t-t_1)-(t-t_1)^2\langle(\Delta\Omega)^2\rangle\right\}.$$

Let us introduce the quantity η

$$\eta = 2T_2\langle(\Delta\Omega)^2\rangle^{\frac{1}{2}} \equiv 2T_2\sigma$$

and consider two extreme cases which are the broad ($\eta \gg 1$) and narrow ($\eta \ll 1$) spread of frequencies. In the former case the law of decay is Lorentzian only for the time interval $\Delta t = t-t_1 \ll \sigma^{-1}$. For $\Delta t \gg \sigma^{-1}$ the decay is mainly Gaussian. In the latter case where $\eta \ll 1$ the decay is Gaussian for $\Delta t \gg \sigma^{-1}$.

Thus, fluctuations of the soft mode frequency can modify the law of decay of the "free induction" signal. One could expect such fluctuations in the vicinity of a critical point.

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