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A Phase - Field Model for the Paraelectric - Ferroelectric Transition

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Abstract

The purpose of the paper is to model the nonlinear relation characterizing the ferroelectric properties of polycrystals and to frame the paraelectric-ferroelectric transition as a classical transition between different phases. The thermodynamic analysis is developed by regarding the polycrystal as a mixture of two phases. The constitutive functions allow for a dependence on the first- and second-order gradient of the polarization. Furthermore the polarization is regarded as an internal variable, which means that its evolution equation is characterized by an unknown constitutive function to be compatible with the thermodynamic requirements. The phase transition is framed within the phase-field model and the order parameter is an internal variable. The advantage of the approach is the unified scheme of constitutive equations and phase transitions.

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1 Introduction

Paraelectric crystals exhibit a linear relation between the electric field $\mathbf{E}$ and the electric polarization $\mathbf{P}$. Ferroelectric crystals show a spontaneous polarization, namely a nonzero $\mathbf{P}$ when $\mathbf{E} = 0$, and also a nonlinear behaviour and hysteretic effects in the $\mathbf{P}$-$\mathbf{E}$ relation. A paraelectric crystal undergoes a change to the ferroelectric state when it is cooled down below a temperature θ_c, called the Curie temperature, thus showing that a transition, from the paraelectric state to the ferroelectric state, has occurred. Above the Curie temperature, the materials are paraelectric in that the relation is linear with a coefficient, the electric susceptibility, which is inversely proportional to the difference $\theta - \theta_c$ between the current temperature θ and θ_c.

The purpose of this paper is twofold. First, to provide the nonlinear relation, characterizing the ferroelectric properties, within a thermodynamic framework. Secondly, to model the paraelectric-ferroelectric transition across θ_c as a classical phase transition.

The thermodynamic analysis is developed by modelling the body as a mixture of two phases or constituents, the paraelectric and the ferroelectric ones. The constitutive functions allow for a dependence on the first- and second-order gradient of $\mathbf{P}$. Consistent with such a non-simple character, a non-zero extra entropy flux is admitted. Furthermore $\mathbf{P}$ is regarded as an internal variable, which means that the evolution equation for $\mathbf{P}$ is characterized by an unknown constitutive function to be compatible with the thermodynamic requirements. For simplicity, the body is regarded as undeformable.

The phase transition is framed within the phase-field model. The order parameter, which describes the transition between the two phases, is taken to occur smoothly, within an appropriate layer or diffuse interface [1, 3]. We follow the view that the order parameter, φ, is an internal variable whose time dependence is subject to the requirements of thermodynamics. There is not a common view, in the literature, about the choice and the role of the order parameter. In [1] φ for the ferroelectric transition is identified with the polarization. Instead, in [10] φ is identified with the volume concentration (or the volume fraction) of the ferroelectric phase. I think that, in general, the appropriate order parameter is a concentration for compressible mixtures [9] or a volume fraction.

The advantage of this approach is the unified scheme of constitutive equations and phase transitions. The dependence of the polarization $\mathbf{P}$ on the state independent variables, as far as all constitutive equations, is characterized by the thermodynamic restrictions. Indeed we find that the time derivative of $\mathbf{P}$ enters an inequality which involves the free energy. Hence we find that the evolution of $\mathbf{P}$ is governed by the appropriate free energy. Motivated by a recent model of ferroelectricity [5], where the evolution equation is in fact a wave equation, a further approach is developed where the second-order time derivative is given by a constitutive function to be characterized.

Notation. Throughout $\mathbb{R}$ and $\mathbb{R}^+$ stand for the reals and the positive reals. An undeformable dielectric body occupies the region $\Omega \subseteq \mathbb{R}^3$. By $\mathbf{x} \in \Omega$ we mean the position vector of a point of the body.

The symbols $\nabla, \nabla\cdot, \nabla\times$ and Δ stand for the gradient, the divergence, the curl and the Laplacian operators whereas ∂_t or a superposed dot denote the time derivative.

2 Balance equations

The electric field $\mathbf{E}$, the magnetic induction $\mathbf{B}$, the electric displacement $\mathbf{D}$ and the magnetic intensity $\mathbf{H}$, on the space-time domain $\Omega \times \mathbb{R}$, satisfy Maxwell's equations

$$\nabla \times \mathbf{E} = -\dot{\mathbf{B}}, \qquad \nabla \times \mathbf{H} = \dot{\mathbf{D}} + \mathbf{J}, \tag{2.1}$$

$$\nabla \cdot \mathbf{B} = 0, \qquad \nabla \cdot \mathbf{D} = \rho, \tag{2.2}$$

where $\mathbf{J}$ is the current density and ρ is the charge density. The balance of energy is based on the view that $\mathbf{E} \times \mathbf{H}$ is the vector flux of energy of electromagnetic character. This view hinges on Poynting's theorem which merely shows that the equation

$$-\nabla \cdot (\mathbf{E} \times \mathbf{H}) = \mathbf{H} \cdot \dot{\mathbf{B}} + \mathbf{E} \cdot \dot{\mathbf{D}} + \mathbf{E} \cdot \mathbf{J} \tag{2.3}$$

follows from Maxwell's equations. Since the body is undeformable the mechanical power vanishes and the balance of energy is taken in the form

$$\dot{e} = -\nabla \cdot (\mathbf{q} + \mathbf{E} \times \mathbf{H}) + r,$$

where e is the energy density (per unit mass) and r is the heat supply. By (2.3) we can write the balance of energy as

$$\dot{e} = \mathbf{H} \cdot \dot{\mathbf{B}} + \mathbf{E} \cdot \dot{\mathbf{D}} + \mathbf{J} \cdot \mathbf{E} - \nabla \cdot \mathbf{q} + r. \tag{2.4}$$

The second law of thermodynamics is taken as the statement that the Clausius-Duhem inequality holds for any set of functions which satisfy Maxwell's equations (2.1)-(2.2) and the energy equation (2.4). Also because of possible nonlocal effects, the entropy flux is likely to be different from $\mathbf{q}/\theta$, θ being the absolute temperature. Hence, letting η be the entropy density and $\mathbf{k}$ the extra-entropy flux vector, we write the Clausius-Duhem inequality in the form

$$\dot{\eta} \geq -\nabla \cdot (\mathbf{q}/\theta) - \nabla \cdot \mathbf{k} + \frac{r}{\theta}. \tag{2.5}$$

By (2.4) and (2.5) we have

$$\dot{e} - \theta\dot{\eta} - \mathbf{H} \cdot \dot{\mathbf{B}} - \mathbf{E} \cdot \dot{\mathbf{D}} - \mathbf{J} \cdot \mathbf{E} + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \theta\nabla \cdot \mathbf{k} \leq 0.$$

The extra entropy flux $\mathbf{k}$ is required to satisfy the boundary condition

$$\int_{\partial\Omega} \mathbf{k} \cdot \mathbf{n}\, da = 0$$

for the whole body. This allows (2.5) to provide the standard global statement

$$\frac{d}{dt}\int_{\Omega} \eta \, dv \geq \int_{\Omega} \frac{r}{\theta} dv - \int_{\partial\Omega} \frac{1}{\theta}\mathbf{q}\cdot\mathbf{n}\, da.$$

Having in mind a model for dielectrics, we disregard the magnetization and let

$$\mathbf{B} = \mu_0 \mathbf{H}, \qquad \mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}.$$

For later convenience we consider the free-energy density $\psi = e - \theta\eta$. Upon substitution we find that the Clausius-Duhem inequality takes the form

$$\dot{\psi} + \eta\dot{\theta} - \mu_0 \mathbf{H}\cdot\dot{\mathbf{H}} - \epsilon_0 \mathbf{E}\cdot\dot{\mathbf{E}} - \mathbf{E}\cdot\dot{\mathbf{P}} - \mathbf{J}\cdot\mathbf{E} + \frac{1}{\theta}\mathbf{q}\cdot\nabla\theta - \theta\nabla\cdot\mathbf{k} \leq 0. \qquad (2.6)$$

Restrictions placed by the inequality (2.6) are now evaluated for a rather general set of constitutive equations.

3 Thermodynamic restrictions

The constitutive assumptions are suggested by the need of accounting for nonlinearities and hysteretic effects of the ferroelectric phase and the bi-stable dynamics of the phase transition. Hence we let $\dot{\mathbf{P}}$ be governed by the independent variables so that the ferroelectric behaviour is modelled. Also, the time derivative $\dot{\varphi}$ of the order parameter φ is assumed to be given by a function which models the phase transition.

Constitutive assumptions. We assume that $\psi, \eta, \mathbf{q}, \mathbf{k}$ and $\dot{\mathbf{P}}, \dot{\varphi}$ are given by continuous functions of the set of variables

$$\Gamma = (\theta, \mathbf{E}, \mathbf{H}, \mathbf{P}, \varphi, \nabla\theta, \nabla\mathbf{P}, \nabla\varphi, \nabla\nabla\theta, \nabla\nabla\mathbf{P}, \nabla\nabla\varphi)$$

and, moreover, ψ is continuously differentiable but is independent on the higher-order gradients $\nabla\nabla\theta, \nabla\nabla\mathbf{P}, \nabla\nabla\varphi$.

Let $\Gamma_1 = (\theta, \mathbf{E}, \mathbf{H}, \mathbf{P}, \varphi, \nabla\theta, \nabla\mathbf{P}, \nabla\varphi)$, the subset of Γ with derivatives up to first-order. Hence $\psi = \psi(\Gamma_1)$. Also, denote by the scalar- and vector-valued functions $f, \mathbf{g}$ the constitutive functions for $\dot{\varphi}$ and $\dot{\mathbf{P}}$, whence

$$\dot{\varphi} = f(\Gamma), \qquad \dot{\mathbf{P}} = \mathbf{g}(\Gamma). \qquad (3.1)$$

To investigate the restrictions placed by (2.6) on the constitutive functions we need to understand the arbitrariness allowed on the fields Γ. Maxwell's equations read

$$\mu_0 \dot{\mathbf{H}} = -\nabla\times\mathbf{E}, \qquad \nabla\times\mathbf{H} = \epsilon_0\dot{\mathbf{E}} + \dot{\mathbf{P}} + \mathbf{J},$$

$$\nabla \cdot \mathbf{H} = 0, \qquad \nabla \cdot \mathbf{E} = 0.$$

As a consequence, we can take the values of $\dot{\mathbf{H}}, \dot{\mathbf{E}}$ as arbitrary whereas $\dot{\mathbf{P}}$ is provided by $\mathbf{g}(\Gamma)$.

The chain rule and use of (3.1) allow us to write (2.6) in the form

$$\begin{aligned}(\psi_\theta + \eta)\dot{\theta} + \psi_{\nabla\theta}\nabla\dot{\theta} + (\psi_{\mathbf{E}} - \epsilon_0\mathbf{E}) \cdot \dot{\mathbf{E}} + (\psi_{\mathbf{H}} - \mu_0\mathbf{H}) \cdot \dot{\mathbf{H}} + (\psi_{\mathbf{P}} - \epsilon_0\mathbf{E}) \cdot \mathbf{g} \\ +\psi_\varphi f + \psi_{\nabla\mathbf{P}} \cdot \nabla\mathbf{g} + \psi_{\nabla\varphi} \cdot \nabla f - \mathbf{J} \cdot \mathbf{E} + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \theta\nabla \cdot \mathbf{k} \leq 0, \quad (3.2)\end{aligned}$$

where the subscripts $\theta, \nabla\theta, \mathbf{E}, \mathbf{H}, \mathbf{P}, \nabla\mathbf{P}, \nabla\varphi$ denote partial derivatives. The arbitrariness of $\dot{\theta}$, $\nabla\dot{\theta}$, and $\dot{\mathbf{H}}$, $\dot{\mathbf{E}}$ requires that

$$\eta = -\psi_\theta, \qquad \psi_{\nabla\theta} = 0, \tag{3.3}$$

and

$$\psi_{\mathbf{H}} = \mu_0\mathbf{H}, \qquad \psi_{\mathbf{E}} = \epsilon_0\mathbf{E}. \tag{3.4}$$

As a consequence,

$$\psi = \frac{1}{2}\mu_0\mathbf{H}^2 + \frac{1}{2}\epsilon_0\mathbf{E}^2 + \Psi(\theta, \mathbf{P}, \varphi, \nabla\mathbf{P}, \nabla\varphi). \tag{3.5}$$

Upon some rearrangements, the inequality (3.2) becomes

$$\begin{aligned}(\Psi_{\mathbf{P}} - \epsilon_0\mathbf{E} - \nabla \cdot \Psi_{\nabla\mathbf{P}}) \cdot \mathbf{g} + \nabla \cdot (\Psi_{\nabla\mathbf{P}}\mathbf{g} + \Psi_{\nabla\varphi} f - \theta\mathbf{k}) \\ +(\Psi_\varphi - \nabla \cdot \Psi_{\nabla\varphi}) f + \mathbf{k} \cdot \nabla\theta - \mathbf{J} \cdot \mathbf{E} + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta \leq 0.\end{aligned} \tag{3.6}$$

Rather than investigating the structure of $\nabla \cdot (\Psi_{\nabla\mathbf{P}}\mathbf{g} + \psi_{\nabla\varphi} f - \theta\mathbf{k})$ we look for a simple scheme compatible with (3.6). We let

$$\theta\mathbf{k} = \Psi_{\nabla\mathbf{P}}\mathbf{g} + \Psi_{\nabla\varphi} f \tag{3.7}$$

so that the divergence is identically zero. Now,

$$(\Psi_{\mathbf{P}} - \epsilon_0\mathbf{E} - \nabla \cdot \Psi_{\nabla\mathbf{P}}) \cdot \mathbf{g} + \frac{1}{\theta}(\Psi_{\nabla\mathbf{P}}\mathbf{g}) \cdot \nabla\theta = [\theta(\hat{\Psi}_{\mathbf{P}} - \nabla \cdot \hat{\Psi}_{\nabla\mathbf{P}}) - \epsilon_0\mathbf{E}] \cdot \mathbf{g},$$

where

$$\hat{\Psi} = \frac{\Psi}{\theta}.$$

Also,

$$(\psi_\varphi - \nabla \cdot \psi_{\nabla\varphi}) f + \frac{1}{\theta}\Psi_{\nabla\varphi} f = \theta(\hat{\Psi}_\varphi - \nabla \cdot \hat{\Psi}_{\nabla\varphi}) \cdot f.$$

Hence, letting

$$\delta_{\mathbf{P}}\hat{\Psi} := \hat{\Psi}_{\mathbf{P}} - \nabla \cdot \hat{\Psi}_{\nabla \mathbf{P}}, \qquad \delta_{\varphi}\hat{\Psi} := \hat{\Psi}_{\varphi} - \nabla \cdot \hat{\Psi}_{\nabla \varphi},$$

we can write (3.6) in the form

$$(\theta \delta_{\mathbf{P}}\hat{\Psi} - \epsilon_0 \mathbf{E}) \cdot \mathbf{g} + \theta \delta_{\varphi}\hat{\Psi}\ f - \mathbf{J} \cdot \mathbf{E} + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta \leq 0. \tag{3.8}$$

The conditions (3.1), (3.3)-(3.5), (3.7), (3.8) are sufficient for the identical validity of (2.6).

The inequality (3.8) holds if each term has the right sign. Such is the case if

$$\mathbf{J} = \Sigma \mathbf{E}, \qquad \mathbf{q} = -\mathbf{K}\nabla\theta,$$

with positive-definite tensors Σ and $\mathbf{K}$, possibly dependent on Γ. This means that the general forms of Ohm's and Fourier's laws are compatible with the thermodynamic requirements. The inequalities

$$(\theta \delta_{\mathbf{P}}\hat{\Psi} - \epsilon_0 \mathbf{E}) \cdot \mathbf{g} \leq 0, \tag{3.9}$$

$$\delta_{\varphi}\hat{\Psi}\ f \leq 0, \tag{3.10}$$

are restrictions on the evolution of $\mathbf{P}$ and φ.

It is worth remarking that $\delta_{\mathbf{P}}\hat{\Psi}$ and $\delta_{\varphi}\hat{\Psi}$ are the variational derivative of the functional

$$F[\theta, \mathbf{P}, \varphi] = \int_{\Omega} \frac{1}{\theta}\Psi(\theta, \mathbf{P}, \varphi, \nabla\mathbf{P}, \nabla\varphi) dv$$

with respect to $\mathbf{P}$ and φ.

4 Restrictions on the evolution equation of P

We now determine sufficient conditions for the validity of (3.9). Let

$$\mathbf{u} = \theta \delta_{\mathbf{P}}\hat{\Psi} - \epsilon_0 \mathbf{E}, \qquad \mathbf{w} = \dot{\mathbf{P}}.$$

The inequality (3.9) can then be written as

$$\mathbf{u} \cdot \mathbf{w} \leq 0. \tag{4.1}$$

Let $\mathbf{v} = \mathbf{u} + \xi \mathbf{P} \times \mathbf{w}, \qquad \xi \in \mathbb{R}$. The inequality (4.1) is equivalent to

$$\mathbf{v} \cdot \mathbf{w} \leq 0 \tag{4.2}$$

and (4.2) holds if

$$\mathbf{w} = -\mathbf{A}\mathbf{v} + \beta \mathbf{P} \times \mathbf{v} + \nu \mathbf{P} \times (\mathbf{P} \times \mathbf{v}),$$

where $\mathbf{A}$ is a positive-definite tensor, $\nu \in \mathbb{R}^+$ and $\beta \in \mathbb{R}$. This is so because, upon substitution, we have

$$\mathbf{v} \cdot \mathbf{w} = -\mathbf{v} \cdot \mathbf{A}\mathbf{v} - \nu |\mathbf{P} \times \mathbf{v}|^2.$$

As a consequence, we can write the following result.
Proposition. *The inequality (3.9) holds if* $\dot{\mathbf{P}}$ *is given by*

$$\dot{\mathbf{P}} = -\mathbf{A}\mathbf{v} + \beta \mathbf{P} \times \mathbf{v} + \nu \mathbf{P} \times (\mathbf{P} \times \mathbf{v}), \qquad \mathbf{v} = \theta \delta_{\mathbf{P}} \hat{\Psi} - \epsilon_0 \mathbf{E} + \xi \mathbf{P} \times \dot{\mathbf{P}}, \tag{4.3}$$

for every positive-definite tensor $\mathbf{A}$, *every* $\nu \in \mathbb{R}^+$ *and every* $\beta, \xi \in \mathbb{R}$.

For definiteness let

$$\Psi = G(\theta, \varphi, \mathbf{P}) + \frac{1}{2} \kappa \theta |\nabla \mathbf{P}|^2.$$

Hence we have

$$\theta \delta_{\mathbf{P}} \hat{\Psi} = G_{\mathbf{P}}(\theta, \varphi, \mathbf{P}) - \kappa \theta \Delta \mathbf{P}.$$

The vector $\mathbf{v}$ takes the form

$$\mathbf{v} = G_{\mathbf{P}}(\theta, \varphi, \mathbf{P}) - \epsilon_0 \mathbf{E} - \kappa \theta \Delta \mathbf{P} + \xi \mathbf{P} \times \dot{\mathbf{P}}.$$

If $\beta, \nu = 0$ then eq. (4.3) gives the evolution equation

$$\dot{\mathbf{P}} = -\mathbf{A}[\xi \mathbf{P} \times \dot{\mathbf{P}} - (\epsilon_0 \mathbf{E} - G_{\mathbf{P}}(\theta, \varphi, \mathbf{P}) + \kappa \theta \Delta \mathbf{P})]. \tag{4.4}$$

In stationary and uniform conditions ($\dot{\mathbf{P}} = 0, \Delta \mathbf{P} = 0$) eq. (4.4) reduces to

$$\epsilon_0 \mathbf{E} = G_{\mathbf{P}}(\theta, \varphi, \mathbf{P}). \tag{4.5}$$

4.1 Relations to other approaches

The evolution equation (4.3) for $\mathbf{P}$ looks very general. The occurrence of $\mathbf{P} \times \dot{\mathbf{P}}$ seems to be new in the literature about ferroelectricity. The analogue, $\mathbf{M} \times \dot{\mathbf{M}}$ occurs in the Gilbert form of the evolution equation for $\mathbf{M}$ in ferromagnetism [4]. Also, it seems that the terms $\mathbf{P} \times \mathbf{v}$ and $\mathbf{P} \times (\mathbf{P} \times \mathbf{v})$ have not been pointed out so far. Anyway, it is remarkable that compatibility of ferroelectricity with thermodynamics holds for the general equation (4.3).

Look now at eq. (4.5). If

$$G = a(\theta - \theta_c)\mathbf{P}^2 + b\mathbf{P}^4, \qquad a, b > 0, \tag{4.6}$$

then **P** and **E** are collinear and

$$\epsilon_0 \mathbf{E} = [2a(\theta - \theta_c) + 4b\mathbf{P}^2]\mathbf{P}. \tag{4.7}$$

The relation (4.7) is a standard model equation of ferroelectricity which traces back to Ginzburg (see [7]) and is the strict analogue of a model of ferromagnetism (see [8]). It is a disadvantage of the potential (4.6) that, for large values of $|\mathbf{P}|$, we have $(4b\mathbf{P}^2)\mathbf{P} = \epsilon_0 \mathbf{E}$ and hence

$$\mathbf{P} = (4b\epsilon_0^2 \mathbf{E}^2)^{-1/3} \epsilon_0 \mathbf{E}.$$

This shows that, according to (4.6), **P** does not attain saturation conditions for large values of $|\mathbf{E}|$.

The model in [2] accounts also for gross motion, which here is disregarded, and ascribes to the continuum a vectorial microstructure. A mathematical difference is due to the simultaneous occurrence, here, of **E** and **P** as independent variables whereas, in [2], **P** is a function of **E**. The ferroelectric behaviour indicates that such dependence is only local.

A thermodynamic approach for deformable ferroelectric crystals is developed in [6]. However the assumption is made that the polarization **P** has a constant magnitude, which strongly influences the constitutive equation for **P**.

5 A free energy potential

In actual ferroelectrects **P** attains a constant saturation value for large values of **E**. On the basis of (4.5) we now look for a free energy G, in uniform conditions, such that the paraelectric and the ferroelectric behaviour are recovered and the saturation value is provided.

Let P_s denote the saturation value of $|\mathbf{P}|$. Let $\varphi \in [0, 1]$ denote the volume fraction (or concentration) of the ferroelectric phase. The dependence of G on **P** is now established so that (4.5) models paraelectricity if $\varphi = 0$ and ferroelectricity if $\varphi = 1$.

Let

$$G(\theta, \varphi, \mathbf{P}) = \frac{1}{2\chi}(1 - \varphi)\mathbf{P}^2 - \frac{1}{2}\varphi[(au + b)\ln(1 - \mathbf{p}^2) + b\mathbf{p}^2] + \mathcal{G}(\theta, \varphi), \tag{5.1}$$

where a, b are positive constants, $a \le b$, and

$$\chi = \frac{\chi_0 \theta_c}{\theta - \theta_c}, \qquad u = \frac{\theta - \theta_c}{\theta_c}, \qquad \mathbf{p} = \frac{\mathbf{P}}{P_s}.$$

As $\varphi = 0$, eq. (4.5) provides

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E}$$

thus ascribing to χ the meaning of dielectric susceptibility. As $\varphi = 1$, eq. (4.5) gives

$$P_s \epsilon_0 \mathbf{E} = \frac{au + b\mathbf{p}^2}{1 - \mathbf{p}^2} \mathbf{p}. \tag{5.2}$$

By (5.2), **E** and **P** are collinear and then we can restrict attention to the significant component E, p in the common direction,

$$P_s \epsilon_0 E = \frac{au + bp^2}{1 - p^2} p, \qquad p \in (-1, 1). \tag{5.3}$$

The remanent or spontaneous polarization, that is the nonzero value P_r of P as $E = 0$, is given at once by (5.3). We have

$$P_r = \pm P_s \frac{a}{b} \frac{\theta_c - \theta}{\theta_c}.$$

The experimental knowledge of P_r, and P_s, provides the ratio a/b.

The coercive electric field, E_c, is the value of E at the local maximum and minimum of p. By (5.3) we have

$$\frac{dE}{dp} = \frac{au + (au + 3b)p^2 - bp^4}{(1 - p^2)^2}. \tag{5.4}$$

Hence we have $dE/dp = 0$ as $p = \pm p_i, \pm p_o$ where

$$p_i^2 = \frac{1}{2}(3 - \frac{a}{b}|u|) - \sqrt{(3 - a|u|/b)^2 - 4a|u|/b},$$

$$p_o^2 = \frac{1}{2}(3 - \frac{a}{b}|u|) + \sqrt{(3 - a|u|/b)^2 - 4a|u|/b}.$$

As we show in a moment, $p_i^2 < 1$ and $p_o^2 > 1$. Hence it follows that only $p_i, -p_i$ are admissible solutions, in $(-1, 1)$. As a consequence the values of the coercive field E_c are given by

$$E_c = \pm \frac{b}{\epsilon_0 P_s} \frac{|p_i|}{1 - p_i^2} (p_i^2 - a|u|/b)$$

and are affected by a/b and b. In conclusion, the knowledge of p_r and E_c allows us to find a/b and b and hence the parameters a and b separately.

We now show that $p_i^2 < 1$. Since $a < b$ then $p_r^2 = |u|a/b < 1$. To prove that $p_i^2 < 1$ we show that

$$3 - p_r^2 - \sqrt{(3 - p_r^2)^2 - 4p_r^2} < 2$$

that is

$$1 - p_r^2 < \sqrt{(3 - p_r^2)^2 - 4p_r^2}.$$

This is so because, squaring both sides, we have

$$1 + 2p_r^2 + p_r^4 < (3 - p_r^2)^2,$$

which is true in that $p_r^2 < 1$.

To show that $p_o^2 > 1$ we observe that $p_o^2 > 1$ is equivalent to

$$3 - p_r^2 + \sqrt{(3 - p_r^2)^2 - 4p_r^2} > 2,$$

namely

$$1 - p_r^2 + \sqrt{(3 - p_r^2)^2 - 4p_r^2} > 0.$$

This inequality is obviously true because of the condition $p_r^2 < 1$.

The function $\mathcal{G}$ is essential in the determination of the entropy function and of the evolution equation for φ. By (5.1) and (3.3) we have

$$\eta = (1 - \varphi)\frac{1}{2\chi_0\theta_c}\mathbf{P}^2 + \varphi\frac{a}{2\theta_c}\ln(1 - \mathbf{p}^2) - \mathcal{G}_\theta. \tag{5.5}$$

Hence the energy density $e = \psi + \theta\eta$ takes the form

$$e = \frac{1}{2}\mu_0\mathbf{H}^2 + \frac{1}{2}\epsilon_0\mathbf{E}^2 - \frac{1}{2\chi_0}(1 - \varphi)\mathbf{P}^2 - \frac{1}{2}\varphi[(b - a)\ln(1 - \mathbf{p}^2) - b\mathbf{p}^2] + \mathcal{E},$$

where

$$\mathcal{E} = \mathcal{G} - \theta\mathcal{G}_\theta.$$

By (3.10) we have

$$\dot{\varphi} = -\kappa\delta_\varphi\hat{\Psi},$$

κ being a positive-valued function of Γ. By disregarding $\nabla\varphi$ dependences, we find that

$$\dot{\varphi} = \kappa[\frac{1}{2\chi}\mathbf{P}^2 + \frac{1}{2}(au + b)\ln(1 - \mathbf{p}^2) - \frac{1}{2}b\mathbf{p}^2 + \mathcal{G}_\varphi]. \tag{5.6}$$

Meanwhile, by (2.4) we have

$$\mathcal{E}_\theta \dot{\theta} + e_\varphi \dot{\varphi} + (e_{\mathbf{P}} - \mathbf{E}) \cdot \dot{\mathbf{P}} = \mathbf{J} \cdot \mathbf{E} - \nabla \cdot \mathbf{q} + r. \tag{5.7}$$

Equations (4.4), (5.6), (5.7) constitute the system of evolution equations for $\mathbf{P}, \varphi, \theta$.

The key point in the proof that $p_i^2 < 1$ and $p_o^2 > 1$ is that $a|u|/b < 1$ as $\theta \in (0, \theta_c)$. A more general, monotone increasing, function u with the same property is

$$u(\theta) = \frac{\theta - \theta_c}{\theta_c}(\frac{b}{a} + c\theta), \qquad c \in [0, b/a\theta_c].$$

It involves an additional parameter, c, and provides $|P_r| \to P_s$ without any requirement on a and b.

5.1 The Curie-Weiss law

In the paraelectric phase, $\theta > \theta_c$, the electric susceptibility obeys the Curie-Weiss law, $\chi \propto (\theta - \theta_c)^{-1}$. This is the obvious consequence of the form (5.1). The Curie-Weiss law holds also for $\theta < \theta_c$ (see [10] and [8] for ferromagnetism). In the ferroelectric phase, $\theta < \theta_c$, only the differential suceptibility dP/dE is meaningful. By (5.4) we have

$$\frac{dP}{dE} = P_s \frac{(1-p^2)^2}{au + (au + 3b)p^2 - bp^4}.$$

As p^2 is around zero we have

$$\frac{dP}{dE} = -\frac{P_s \theta_c}{a} \frac{1}{\theta_c - \theta}.$$

In particular $dP/dE < 0$, and this happens in the unstable part of the $P - E$ curve. The proportionality to $(\theta_c - \theta)^{-1}$ is affected more and more as p^2 increases. Indeed, $dP/dE = 0$ as $E = E_c$ and $dP/dE > 0$ as $E^2 > E_c^2$.

5.2 Latent heat

The phase transition occurs at the temperature θ_c and hence the latent heat λ is related to the entropy function $\eta(\theta, \mathbf{P}, \varphi)$ by

$$\lambda = \theta_c[\eta(\theta_c, \mathbf{P}, 1) - \eta(\theta_c, \mathbf{P}, 0)].$$

By (5.5) we have

$$\lambda = \frac{1}{2}[a \ln(1 - \mathbf{p}^2) - \frac{1}{\chi_0}\mathbf{P}^2] + \theta_c[\mathcal{G}_\theta(\theta_c, 0) - \mathcal{G}_\theta(\theta_c, 1)].$$

There are two contributions to λ, one from the change of the electrical content ($\mathbf{P}$), the other from the change of the chemical content ($\mathcal{G}_\theta$). In [10] the entropy consists of the chemical content only.

6 A second-order evolution equation

A recent model of ferroelectricity [5] involves a second-order evolution equation for the polarization $\mathbf{P}$. They argue as follows. The polarization is regarded as an internal variable which evolves through

$$\epsilon_1(\dot{\mathbf{P}} + \frac{1}{d}\mathbf{l}) = \nabla \times \mathbf{m}$$

while

$$\mu_1(\dot{\mathbf{m}} + \frac{a}{d}\mathbf{m}) = -\nabla \times \mathbf{P}.$$

Here $\mathbf{m}$ has the interpretation of an internal magnetic field and $\mathbf{l}$ is a current density which is driven by the difference between an equilibrium electric field, $\tilde{\mathbf{E}}(\mathbf{P})$, and the electric field $\mathbf{E}$, that is

$$\dot{\mathbf{l}} + \frac{a}{d}\mathbf{l} = \frac{b}{d}[\tilde{\mathbf{E}}(\mathbf{P}) - \mathbf{E}].$$

Upon substitution it follows that $\mathbf{P}$ is governed by the second-order differential equation

$$d^2[\ddot{\mathbf{P}} + \frac{1}{\epsilon_1\mu_1}\nabla \times (\nabla \times \mathbf{P})] + ad\dot{\mathbf{P}} = b[\mathbf{E} - \tilde{\mathbf{E}}(\mathbf{P})]. \tag{6.1}$$

We now examine how a second-order differential equation for $\mathbf{P}$ can arise from a thermodynamic scheme without involving additional internal fields $\mathbf{l}, \mathbf{m}$ which do not seem to have an operative physical meaning.

We parallel the analysis of §4 though with more involved constitutive assumptions. We let $\dot{\mathbf{P}}$ and $\nabla\dot{\mathbf{P}}$ enter the independent variables so that

$$\Gamma = (\theta, \mathbf{E}, \mathbf{H}, \mathbf{P}, \varphi, \nabla\theta, \nabla\mathbf{P}, \dot{\mathbf{P}}, \nabla\varphi, \nabla\nabla\theta, \nabla\nabla\mathbf{P}, \nabla\dot{\mathbf{P}}, \nabla\nabla\varphi)$$

is the set of independent variables.
Constitutive assumptions. We assume that $\eta, \mathbf{q}, \mathbf{k}$ and $\ddot{\mathbf{P}}, \dot{\varphi}$ are continuous functions of Γ whereas ψ is continuously differentiable but is independent of the higher-order derivatives $\nabla\nabla\theta$, $\nabla\nabla\mathbf{P}, \nabla\dot{\mathbf{P}}, \nabla\nabla\varphi$.

Denote by $\mathbf{h}$ and f the constitutive functions for $\ddot{\mathbf{P}}$ and $\dot{\varphi}$,

$$\ddot{\mathbf{P}} = \mathbf{h}(\Gamma), \qquad \dot{\varphi} = f(\Gamma). \tag{6.2}$$

The arbitrariness of $\dot{\theta}, \nabla\dot{\theta}, \dot{\mathbf{H}}, \dot{\mathbf{E}}$ holds again and provides eqs (3.3) and (3.4) so that

$$\psi = \frac{1}{2}\mu_0\mathbf{H}^2 + \frac{1}{2}\epsilon_0\mathbf{E}^2 + \Psi(\theta, \mathbf{P}, \varphi, \nabla\mathbf{P}, \dot{\mathbf{P}}, \nabla\varphi). \tag{6.3}$$

Hence the Clausius-Duhem inequality (2.6) becomes

$$\begin{aligned}&(\Psi_{\mathbf{P}} - \epsilon_0 \mathbf{E} - \nabla \cdot \Psi_{\nabla \mathbf{P}}) \cdot \dot{\mathbf{P}} + \Psi_{\dot{\mathbf{P}}} \cdot \mathbf{h} + (\Psi_\varphi - \nabla \cdot \Psi_{\nabla\varphi}) f \\ &+ \nabla \cdot (\Psi_{\nabla \mathbf{P}} \mathbf{g} + \Psi_{\nabla\varphi} f - \theta \mathbf{k}) + \mathbf{k} \cdot \nabla\theta - \mathbf{J} \cdot \mathbf{E} + \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta \leq 0. \qquad (6.4)\end{aligned}$$

We let (3.7) hold whence $\nabla \cdot (\Psi_{\nabla \mathbf{P}} \mathbf{g} + \Psi_{\nabla\varphi} f - \theta \mathbf{k}) = 0$ identically. Hence we have

$$\begin{aligned}&(\Psi_{\mathbf{P}} - \epsilon_0 \mathbf{E} - \nabla \cdot \Psi_{\nabla \mathbf{P}}) \cdot \dot{\mathbf{P}} + (\Psi_\varphi - \nabla \cdot \Psi_{\nabla\varphi}) f + \mathbf{k} \cdot \nabla\theta \\ &= [\Psi_{\mathbf{P}} - \epsilon_0 \mathbf{E} - \nabla \cdot (\Psi_{\nabla \mathbf{P}}/\theta)] \cdot \dot{\mathbf{P}} + [\Psi_\varphi - \nabla \cdot (\Psi_{\nabla\varphi}/\theta)] f.\end{aligned}$$

Letting again $\hat{\Psi} = \frac{\Psi}{\theta}$ and using the derivatives $\delta_{\mathbf{P}}\hat{\Psi}$ and $\delta_\varphi\hat{\Psi}$ we can write (6.4) as

$$(\theta \delta_{\mathbf{P}} \hat{\Psi} - \epsilon_0 \mathbf{E}) \cdot \dot{\mathbf{P}} + \Psi_{\dot{\mathbf{P}}} \cdot \mathbf{h} + \theta \delta_\varphi \hat{\Psi}\, f - \mathbf{J} \cdot \mathbf{E} + \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta \leq 0. \qquad (6.5)$$

Incidentally, because of the occurrence of $\dot{\mathbf{P}}$, $\delta_{\mathbf{P}}\hat{\Psi}$ is no longer the variational derivative of $\hat{\Psi}$ with respect to $\mathbf{P}$.

The inequality (6.5) holds if

$$\delta_\varphi \hat{\Psi}\, f \geq 0, \qquad \mathbf{J} \cdot \mathbf{E} \geq 0, \qquad \mathbf{q} \cdot \nabla\theta \leq 0, \qquad (6.6)$$

as in §4, and

$$(\theta \delta_{\mathbf{P}} \hat{\Psi} - \epsilon_0 \mathbf{E}) \cdot \dot{\mathbf{P}} + \Psi_{\dot{\mathbf{P}}} \cdot \mathbf{h} \leq 0. \qquad (6.7)$$

Of course the new inequality (6.7), which is affected by the dependence of Ψ on $\dot{\mathbf{P}}$, holds if the left-hand side is negative definite. In particular, (6.7) holds if

$$(\theta \delta_{\mathbf{P}} \hat{\Psi} - \epsilon_0 \mathbf{E}) \cdot \dot{\mathbf{P}} + \Psi_{\dot{\mathbf{P}}} \cdot \mathbf{h} = -\gamma \dot{\mathbf{P}}^2, \qquad (6.8)$$

γ being a positive-valued function of Γ. The conditions (3.3), (3.4) and (6.2)-(6.4), (3.7), (6.6), (6.8) are sufficient for the identical validity of the Clausius-Duhem inequality (2.6).

We now show that (6.1) is an evolution equation compatible with, or a particular case of, (6.8). To this end we observe that if $\hat{\Psi}$ depends on $\nabla\mathbf{P}$ through $\nabla \times \mathbf{P}$ then

$$\nabla \cdot \hat{\Psi}_{\nabla \mathbf{P}} = -\nabla \times \hat{\Psi}_{\nabla \times \mathbf{P}}. \qquad (6.9)$$

In suffix notation, letting ϵ_{jkh} be the permutation symbol we have

$$\frac{\partial \hat{\Psi}}{\partial P_{k,j}} = \frac{\partial \hat{\Psi}}{\partial (\nabla \times \mathbf{P})_h} \frac{\partial (\nabla \times \mathbf{P})_h}{\partial P_{k,j}} = \epsilon_{jkh} \frac{\partial \hat{\Psi}}{\partial (\nabla \times \mathbf{P})_h}$$

and hence

$$\frac{\partial}{\partial x_j}\frac{\partial \hat{\Psi}}{\partial P_{k,j}} = -\epsilon_{kjh}\frac{\partial}{\partial x_j}\frac{\partial \hat{\Psi}}{\partial (\nabla \times \mathbf{P})_h},$$

which is the k-th component of (6.9).

As a choice, let

$$\Psi(\theta, \mathbf{P}, \varphi, \nabla \mathbf{P}, \dot{\mathbf{P}}, \nabla\varphi) = \bar{\Psi}(\theta, \mathbf{P}, \varphi, \nabla\varphi) + \frac{1}{2}\kappa\theta|\nabla \times \mathbf{P}|^2 + \frac{1}{2}\lambda\dot{\mathbf{P}}^2,$$

where $\kappa, \lambda > 0$. As a consequence,

$$\theta\delta_{\mathbf{P}}\hat{\Psi} = \bar{\Psi}_{\mathbf{P}} + \kappa\theta\nabla \times (\nabla \times \mathbf{P}), \qquad \Psi_{\dot{\mathbf{P}}} = \lambda\dot{\mathbf{P}}.$$

Hence (6.8) becomes

$$[\hat{\Psi}_{\mathbf{P}} - \epsilon_0\mathbf{E} + \theta\kappa\nabla \times (\nabla \times \mathbf{P}) + \lambda\ddot{\mathbf{P}} + \gamma\dot{\mathbf{P}}] \cdot \dot{\mathbf{P}} = 0$$

which is the inner product with $\dot{\mathbf{P}}$ of

$$\lambda[\ddot{\mathbf{P}} + \frac{\theta\kappa}{\lambda}\nabla \times (\nabla \times \mathbf{P})] + \gamma\dot{\mathbf{P}} = \epsilon_0(\mathbf{E} - \frac{1}{\epsilon_0}\bar{\Psi}_{\mathbf{P}}). \tag{6.10}$$

The identification of (6.10) with (6.1) is complete. Indeed, we see that the equilibrium electric field $\tilde{\mathbf{E}}(\mathbf{P})$ [5] is to be identified with $\bar{\Psi}_{\mathbf{P}}/\epsilon_0$.

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