Chapter 2

Advances in Thermodynamics of Ferroelectric Phase Transitions

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/52089

1. Introduction

The thermodynamics of ferroelectric phase transitions is an important constituent part of the phenomenological theories of them, as well as the interface dynamics of them. In particular, if we confine the thermodynamics to the equilibrium range, we can say that the Landau-Devonshire theory is a milestone in the process of the development of ferroelectric phase transition theories. This can be found in many classical books such as [1,2]. Many studies centering on it, especially the size-effects and surface-effects of ferroelectric phase transitions, have been carried out. For the reason of simplicity, we just cite a few [3,4]. But we think these are a kind of technical but not fundamental progress.

Why we think so is based on that the Landau-Devonshire theory is confined to the equilibrium range in essene so it can't deal with the outstanding irreversible phenomonon of first-order ferroelectric phase transitions strictly, which is the „thermal hysteresis". The Landau-Devonshire theory attributes the phenomenon to a series of metastable states existing around the Curie temperature T_C. In principle, the metastable states are not the equilibrium ones and can not be processed by using the equilibrium thermodynamics. Therefore, we believe the Landau-Devonshire theory is problematic though it is successful in mathematics. The real processes of phase transition were distorted. In this contribution, the Landau-Devonshire theory will be reviewed critically, then the latest phenomenological theory of ferroelectric phase transitions will be established on the basis of non-equilibrium or irreversible thermodynamics.

This contribution are organized as the follows. In Section 2, we will show the unpleasant consequence caused by the metastable states hypothesis, and the evidence for the non-existence of metastable states, i.e. the logical conflict. Then in Section 3 and 4, we will give the non-equilibrium (or irreversible) thermodynamic description of ferroelectric phase transi-

tions, which eliminates the unpleasant consequence caused by the metastable states hypothesis. In Section 5, we will give the non-equilibrium thermodynamic explanation of the irreversibility of ferroelectric phase transitions, i.e. the thermal hysteresis and the domain occurrences in ferroelectrics. At last, in Section 6 we will make some concluding remarks and look forward to some possible developments.

2. Limitations of Landau-Devonshire theory and demonstration of new approach

The most outstanding merit of Landau-Devonshire theory is that the Curie temperature and the spontaneous polarization at Curie temperature can be determined simply. However, in the Landau-Devonshire theory, the path of a first-order ferroelectric phase transition is believed to consist of a series of metastable states existing around the Curie temperature. This is too difficult to believe because of the difficulties encounted (just see the follows) T_C.

2.1. Unpleasant consequence caused by metastable states hypothesis

Basing on the Landau-Devonshire theory, we make the following inference. Because of the thermal hysteresis, a first-order ferroelectric phase transition must occur at another temperature, which is different from the Curie temperature [5]. The state corresponding to the mentioned temperature (i.e. actural phase transition temperature) is a metastable one. Since the unified temperature and spontanous polarization can be said about the metastable state, we neglect the heterogeneity of system actually. In other words, every part of the system, i.e. either the surface or the inner part, is of equal value physically. When the phase transition occurs at the certain temperature, every part of the system absorbs or releases the latent heat simultaneously by a kind of action at a distance. (The concept arose in the electromagnetism first. Here it maybe a kind of heat transfer.) Otherwise, the heat transfer in system, with a finite rate, must destroy the homogeneity of system and lead to a non-equilibrium thermodynamic approach. The unpleasant consequence, i.e. the action at a distance should be eliminated and the lifeforce should be bestowed on the non-equilibrium thermodynamic approach.

In fact, a first-order phase transition process is always accompanied with the fundamental characteristics, called the co-existence of phases and the moving interface (i.e. phase boundary). The fact reveals that the phase transition at various sites can not occur at the same time. Yet, the phase transition is induced by the external actions (i.e. absorption or release of latent heat). It conflicts sharply with the action at a distance.

2.2. Evidence for non-existence of metastable states: logical conflict

In the Landau-Devonshire theory, if we neglect the influence of stress, the elastic Gibbs energy G_1 can be expressed with a binary function of variables, namely the temperature T and the electric displacement D (As G_1 is independent of the orientation of D, here we are interested in the magnitude of D only)

$$G_1 = g_1\left(T, D\right) \tag{1}$$

The long-standing, close correlation between analytical dynamics and thermodynamics implies that Equation (1) can be taken as a scleronomic constraint equation

$$f_1\left(G_1, T, D\right) = G_1 - g_1\left(T, D\right) = 0 \tag{2}$$

where G_1, T, D are the generalized displacements. The possible displacements $\mathrm{d}G_1$, $\mathrm{d}T$ and $\mathrm{d}D$ satisfy the following equation

$$\mathrm{d}G_1 - \frac{\partial g_1}{\partial T}\mathrm{d}T - \frac{\partial g_1}{\partial D}\mathrm{d}D = 0 \tag{3}$$

In the Landau-Devonshire theory, the scleronomic constraint equation, i.e. Equation (1) is expressed in the form of the power series of D (For simplicity, only the powers whose orders are not more than six are considered)

$$G_1 = G_{10} + \frac{1}{2}\alpha D^2 + \frac{1}{4}\beta D^4 + \frac{1}{6}\gamma D^6 \tag{4}$$

where α, β, γ are the functions of T, and G_{10} is the elastic Gibbs energy of paraelectric phase. The relation between G_1 and D at various temperature, which belongs to first-order phase transition ferroelectrics is represented graphically in Figure 1. The electric displacements which correspond to the bilateral minima of G_1 are identified as $\pm D^*$, and the electric displacement which corresponds to the middle minimum of G_1 equals zero. The possible electric displacements should be the above ones which correspond to the minima of G_1.

Equivalently, imposed on the generalized displacements G_1, T, D is a constraint, which is

$$\frac{\partial G_1}{\partial D} = 0 \tag{5}$$

So, the possible displacement $\mathrm{d}D$ should be the follows $\mathrm{d}D^*$, $-\mathrm{d}D^*$, $0-\left(\pm D^*\right) = \mp D^*$, $\pm D^* - 0 = \pm D^*$, 0. After all, if our discussion are limited in the equilibrium thermodynamics strictly, there must be the third constraint, i.e. the equilibrium D and T should satisfy

$$h\left(D, T\right) = 0 \tag{6}$$

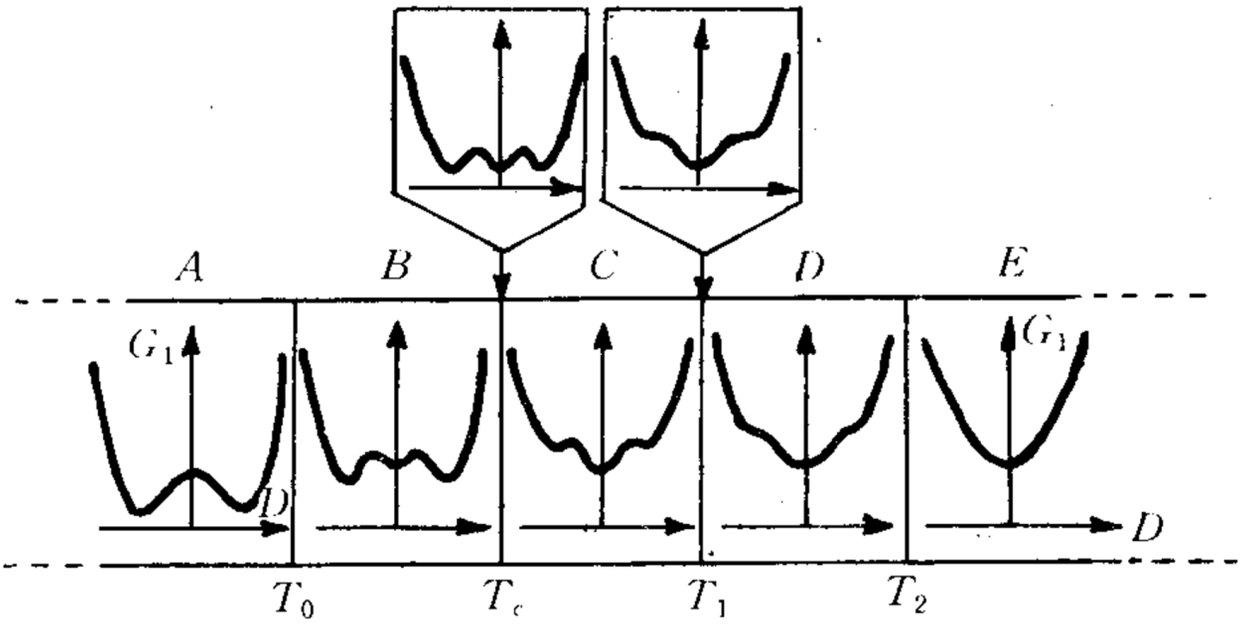

Figure 1. The relation between elastic Gibbs energy G_1 and zero field electric displacement D belongs to the ferroelectrics at various temperature, which undergoes a first-order phase transition [5]. T_0 :the lowest temperature at which the paraelectric phase may exist, i.e. the Curie-Weiss temperature; T_C :the phase transition temperature, i.e. the Curie temperature; T_1 : the highest temperature at which the ferroelectric phase may exist; T_2 : the highest temperature at which the ferroelectric phase may be induced by the external electric field.

where h is a binary function of the variables D and T. It can be determined by the principle of minimum energy

$$G_1 = \min \tag{7}$$

for certain T. Then, the metastable states are excluded. Thus, the thermal hysteresis does not come into being. The corollary conflicts with the fact sharply. This reveals that the first-order ferroelectric phase transition processes must not be reversible at all so as not to be dealt with by using the equilibrium thermodynamics.

How can this difficulty be overcome? An expedient measure adopted by Devonshire is that the metastable states are considered. However, do they really exist?

Because the metastable states are not the equilibrium ones, the relevant thermodynamic variables or functions should be dependent on the time t. In addition, the metastable states are close to equilibrium, so the heterogeneity of system can be neglected. Here, the elastic Gibbs energy G'_1 should be

$$G'_1 = g_2(T, D, t) \tag{8}$$

For the same reason as was mentioned above, Equation (8) can be regarded as a rheonomic constraint on the generalized displacements G'_1, T, D

$$f_2\left(G_1',T,D,t\right)=G_1'-g_2\left(T,D,t\right)=0 \tag{9}$$

In this case, the possible displacements $\mathrm{d}G_1'$, $\mathrm{d}T$ and $\mathrm{d}D$ satisfy the following equation

$$\mathrm{d}G_1'-\frac{\partial g_2}{\partial T}\mathrm{d}T-\frac{\partial g_2}{\partial D}\mathrm{d}D-\frac{\partial g_2}{\partial t}\mathrm{d}t=0 \tag{10}$$

Comparing Equation (3) with Equation (10), we may find that the possible displacements here are not the same as those in the former case which characterize the metastable states for they satisfy the different constraint equations, respectively. (In the latter case, the possible displacements are time-dependent, whereas in the former case they are not.) Yet, the integral of possible displacement $\mathrm{d}D$ is the possible electric displacement in every case. The possible electric displacements which characterize one certain metastable state vary with the cases. A self-contradiction arises. So the metastable states can not come into being.

What are the real states among a phase transition process? In fact, both the evolution with time and the spatial heterogeneity need to be considered when the system is out of equilibrium [6-9]. Just as what will be shown in Section 2.3, the real states should be the stationary ones, which do not vary with the time but may be not metastable.

2.3. Real path: Existence of stationary states

The real path of a first-order ferroelectric phase transition is believed by us to consist of a series of stationary states. At first, this was conjectured according to the experimental results, then was demonstrated reliable with the aid of non-equilibrium variational principles.

Because in the experiments the ferroelectric phase transitions are often achieved by the quasi-static heating or cooling, we conjetured that they are stationary states processes [8]. The results on the motion of interface in ferroelectrics and antiferroelectrics support our opinion [10-12]. From Figure 2, we may find that the motion of interface is jerky especially when the average velocity v_a is small. A sequence of segments of time corresponding to the states of rest may be found. The experimental results about other materials such as $PbTiO_3$ are alike [11]. This reveals that in these segments of time (i.e. characteristic time of phase transition) the stationary distributions of temperature, heat flux, stress, etc. may be established. Otherwise, if the motion of interface is continuous and smooth, with the unceasing moving of interface (where the temperature is T_C) to the inner part, the local temperature of outer part must change to keep the temperature gradient ∇T of this region unchanged for it is determined by $\pm l\rho v'=J_q^{diff}=-\kappa\nabla T$, where l is the latent heat (per unit mass), ρ is the mass density, v' is the velocity of interface (where the phase transition is occurring), J_q^{diff} is the diffusion of heat, i.e. heat conduction, κ is the thermal conductivity (and maybe a tensor.) Then, the states are not stationary.

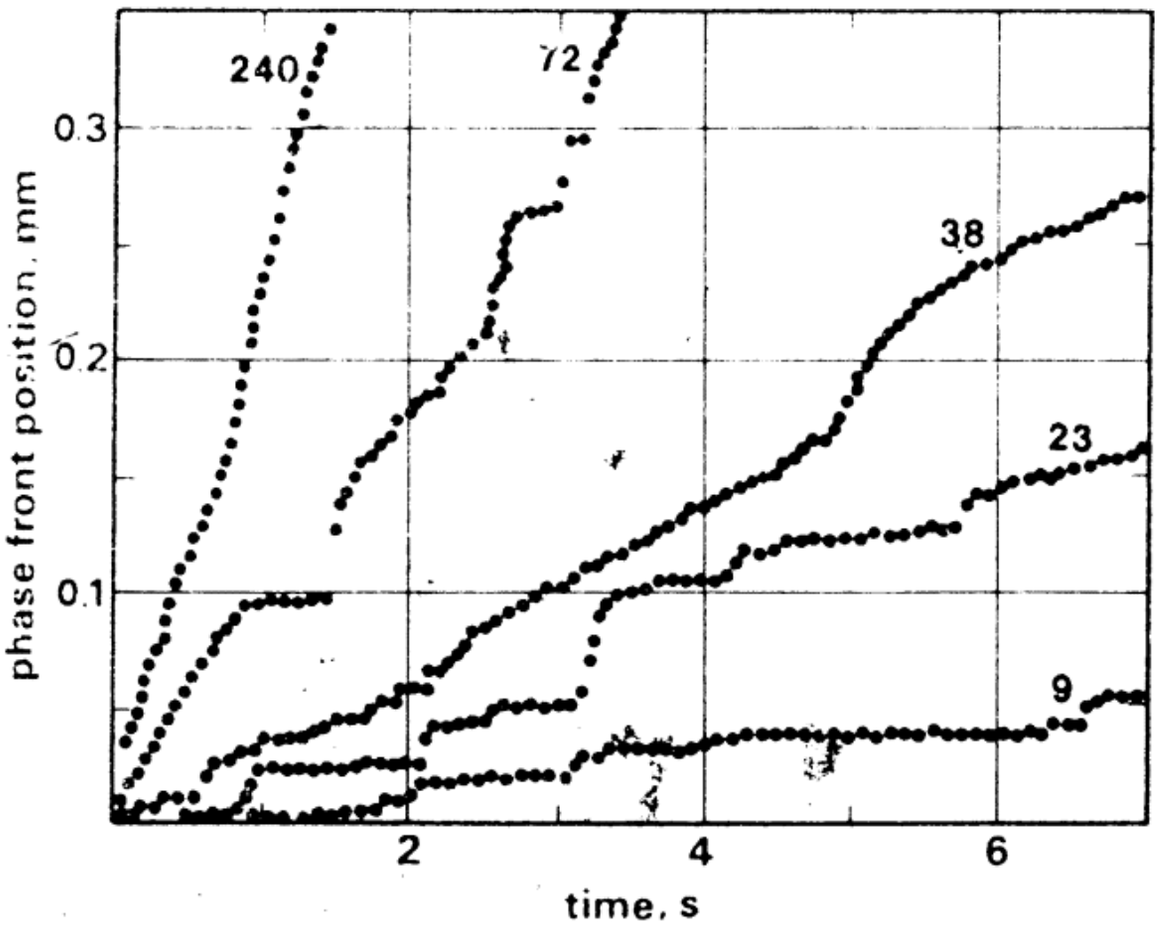

Figure 2. The position of phase boundary as a function of time for $NaNbO_3$ single crystal for the various values of average velocity v_a (the values in μm/s given against the curves) [12].

The non-equilibrium variational principles are just the analogue and generalization of the variational principles in analytical dynamics. The principle of least dissipation of energy, the Gauss's principle of least constraint and the Hamiltonian principle etc., in non-equilibrium thermodynamics play the fundamental roles as those in analytical dynamics. They describe the characteristics of stationary states or determine the real path of a non-equilibrium process.

For the basic characteristics of non-equilibrium processes is the dissipation of energy, the dissipation function φ is defined as

$$\varphi = \sigma_s - \pi \tag{11}$$

where σ_s is the rate of local entropy production and π is the external power supply (per unit volume and temperature). After the rather lengthy deducing and utilizing the thermodynamic Gauss's principle of least constraint which makes the system choose a real path [13], the evolution with time t of the deviation from a given non-equilibrium stationary state, $\xi(t)=\{\xi_i(t)\}$, was obtained in two cases. If no external power supply,

http://dx.doi.org/10.5772/52089

$$\xi_i(t) = \xi_i(0) e^{\frac{2S_i}{R_i}t} \tag{12}$$

where $\xi_i(0)$ is the initial value of $\xi_i(t)$, S_i is the coefficient between the linear variation in the thermodynamic force $\chi_{Ti}^{(1)}(\xi)$ and the deviation of the extensive pseudo-thermodynamic variable from a given non-equilibrium stationary state ξ_i, R_i is the coefficient between the linear variation in the dissipative force $\chi_{Di}^{(1)}(\xi)$ and the time-derivative of the deviation of the extensive pseudo-thermodynamic variable from a given non-equilibrium stationary state ξ_i. Equation (12) define the real path with the addition that R_i should be a suitable value R_i^*. If the external power supply exists, similarly the evolution of deviation ξ_i can be obtained

$$\xi_i(t) = \xi_i(0) e^{\frac{2(S_i - V_i)}{R_i}t} \tag{13}$$

where V_i is the coefficient between the linear variation in the force related to the external power $\chi_{Ei}^{(1)}$ and the deviation of the extensive pseudo-thermodynamic variable from a given non-equilibrium stationary state ξ_i. If the coefficients V_i, R_i assume the suitable values V_i^{**}, R_i^{**}, the system choose a real path.

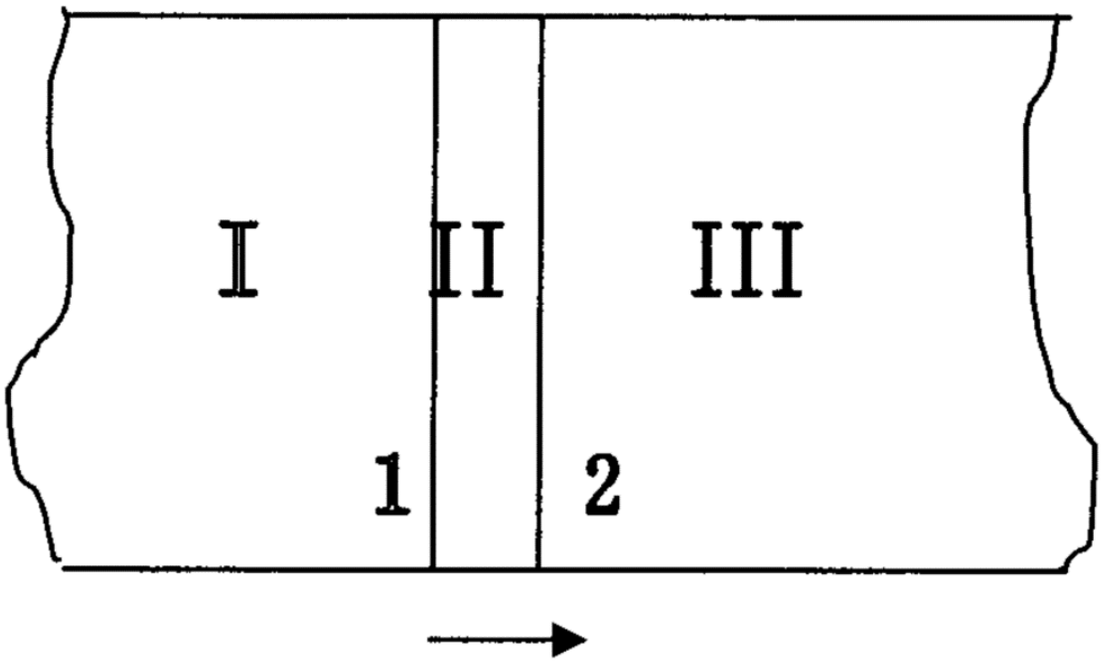

Figure 3. Three types of regions and their interfaces in the ferroelectric-paraelectric system in which a first-order phase transition is occurring [13].

Both the real paths in the two cases reveal that the deviations decrease exponentially when the system regresses to the stationary states. Stationary states are a king of attractors to non-equilibrium states. The decreases are steep. So the regressions are quick. It should be noted that we are interested in calculating the change in the generalized displacements during a macroscopically small time interval. In other words, we are concerned with the determination of the path of an irreversible process which is described in terms of a finite difference equation. In the limit as the time interval is allowed to approach zero, we obtain the variational equation of thermodynamic path.

So, if the irreversible process is not quick enough, it can be regarded as the one that consists of a series of stationary states. The ferroelectric phase transitions are usually achieved by the quasi-static heating or cooling in the experiments. So, the processes are not quick enough to make the states deviate from the corresponding stationary states in all the time. In Figure 3, three types of regions and their interfaces are marked with I, II, III, 1, 2 respectively. The region III where the phase transition will occur is in equilibrium and has no dissipation. In the region I where the phase transition has occurred, there is no external power supply, and in the region II (i.e. the paraelectric-ferroelectric interface as a region with finite thickness instead of a geometrical plane) where the phase transition is occurring, there exists the external power supply, i.e. the latent heat (per unit volume and temperature). According to the former analysis in two cases, we may conclude that they are in stationary states except for the very narrow intervals of time after the sudden lose of phase stability.

3. Thermo-electric coupling

In the paraelectric-ferroelectric interface dynamics induced by the latent heat transfer [6,7], the normal velocity of interface v_n was obtained

$$v_n = \frac{1}{l\rho}\left[k_{fer}\left(\nabla T\right)_{fer} - k_{par}\left(\nabla T\right)_{par}\right]\cdot \boldsymbol{n} \tag{14}$$

where l is the latent heat (per unit mass), ρ is the density of metastable phase (paraelectric phase), k_{fer} is the thermal conductivity coefficient of ferroelectric phase, k_{par} is the thermal conductivity coefficient of paraelectric phase, $(\nabla T)_{fer}$ is the temperature gradient in ferro-electric phase part, $(\nabla T)_{par}$ is the temperature gradient in paraelectric phase part, n is the unit vector in normal direction and directs from the ferroelectric phase part to the paraelectric phase part. The temperature gradients can be studied from the point of view that a ferroelectric phase transition is a stationary, thermo-electric coupled transport process [8].

3.1. Local entropy production

In the thermo-electric coupling case, the Gibbs equation was given as the following [8]

$$T\mathrm{d}s = \mathrm{d}u - \boldsymbol{E}\cdot\mathrm{d}\boldsymbol{D} - \sum_i \mu_i \mathrm{d}n_i \tag{15}$$

where T, E, D is the temperature, the electric field intensity and the electric displacement within a random small volume, respectively; s, u, μ_i, n_i is the entropy density, the internal energy density, the chemical potential and the molar quantity density in the small volume, respectively. And there, it was assumed that the crystal system is mechanically-free (i.e. no force is exerted on it). Differentiating Equation (15) and using the following relations

$$\frac{\partial u}{\partial t} + \nabla\cdot\boldsymbol{J}_u = 0 \tag{16}$$

$$\frac{\partial \boldsymbol{D}}{\partial t} = \frac{\partial\left(\varepsilon_0\boldsymbol{E} + \boldsymbol{P}\right)}{\partial t} = \boldsymbol{J}_P \tag{17}$$

$$\frac{\partial n_i}{\partial t} + \nabla\cdot\boldsymbol{J}_{ni} = 0 \tag{18}$$

we have

$$\frac{\partial s}{\partial t} = -\frac{1}{T}\nabla\cdot\boldsymbol{J}_u - \frac{\boldsymbol{E}}{T}\cdot\boldsymbol{J}_P + \sum_i \frac{\mu_i}{T}\nabla\cdot\boldsymbol{J}_{ni} \tag{19}$$

where J_u, J_P, J_{ni} is the energy flux, the polarization current and the matter flux; P is the polarization. J_u should consist of three parts: the energy flux caused by the heat conduction, the energy flux caused by the charge transport and the energy flux caused by the matter transport

$$\boldsymbol{J}_u = \boldsymbol{J}_q + \varphi\boldsymbol{J}_P + \sum_i \mu_i \boldsymbol{J}_{ni} \tag{20}$$

where J_q is the heat flux, φ is the electrical potential and satisfies

$$\boldsymbol{E} = -\nabla\varphi \tag{21}$$

Then we deduce the following

$$\frac{\partial s}{\partial t} = -\nabla \cdot \left(\frac{\boldsymbol{J}_q + \varphi \boldsymbol{J}_P}{T} \right) + \boldsymbol{J}_q \cdot \nabla \left(\frac{1}{T} \right) + \boldsymbol{J}_P \cdot \nabla \left(\frac{\varphi}{T} \right) - \sum_i \frac{\boldsymbol{J}_{ni}}{T} \cdot \nabla \mu_i \tag{22}$$

If we define a entropy flux J_s and a rate of local entropy production σ_s as

$$\boldsymbol{J}_s = \frac{\boldsymbol{J}_q + \varphi \boldsymbol{J}_P}{T} \tag{23}$$

$$\sigma_s = \boldsymbol{J}_q \cdot \nabla \left(\frac{1}{T} \right) + \boldsymbol{J}_P \cdot \nabla \left(\frac{\varphi}{T} \right) - \sum_i \frac{\boldsymbol{J}_{ni}}{T} \cdot \nabla \mu_i \tag{24}$$

Equation (22) can be written as

$$\frac{\partial s}{\partial t} + \nabla \cdot \boldsymbol{J}_s = \sigma_s \tag{25}$$

This is the local entropy balance equation. We know, the system is in the crystalline states before and after a phase transition so that there is no diffusion of any kind of particles in the system. So, J_{ni}=0. The local entropy production can be reduced as

$$\sigma_s = \boldsymbol{J}_q \cdot \nabla \left(\frac{1}{T} \right) + \boldsymbol{J}_P \cdot \nabla \left(\frac{\varphi}{T} \right) \tag{26}$$

We know the existence of ferroics is due to the molecular field. It is an internal field. So we must take it into account. Here, the electric field should be the sum of the external electric field E_e and the internal electric field E_i

$$\boldsymbol{E} = \boldsymbol{E}_e + \boldsymbol{E}_i \tag{27}$$

Correspondingly, there are the external electrical potential φ_e and the internal electrical potential φ_i and they satisfy

$$\boldsymbol{E}_e = -\nabla \varphi_e \tag{28}$$

$$\boldsymbol{E}_i = -\nabla \varphi_i \tag{29}$$

If the external electric field is not applied, φ_e can be a random constant. There is no harm in letting the constant equal zero. Then the entropy production equals

$$\sigma_s = \boldsymbol{J}_q \cdot \nabla\left(\frac{1}{T}\right) + \boldsymbol{J}_P \cdot \nabla\left(\frac{\varphi_i}{T}\right) \tag{30}$$

According to the crystal structures of ferroelectrics [2], we know the polarization current J_P originates from the displacement or ordering of ions in ferroelectrics. We may consider it as the transport of charges influenced by the internal electric field.

3.2. Description of phase transitions and verification of interface dynamics

Assume the external electric field is not applied. Here are the thermodynamic fluxex J_q, J_P and the corresponding thermodynamic forces X_q, X_P

$$\boldsymbol{X}_q = \nabla\left(\frac{1}{T}\right) \tag{31}$$

$$\boldsymbol{X}_P = \nabla\left(\frac{\varphi_i}{T}\right) \tag{32}$$

J_i can be expanded linearly with $X_j (i,\ j=q,\ P)$

$$\boldsymbol{J}_q = \boldsymbol{L}_{qq} \cdot \boldsymbol{X}_q + \boldsymbol{L}_{qP} \cdot \boldsymbol{X}_P \tag{33}$$

$$\boldsymbol{J}_P = \boldsymbol{L}_{Pq} \cdot \boldsymbol{X}_q + \boldsymbol{L}_{PP} \cdot \boldsymbol{X}_P \tag{34}$$

where L_{qq}, L_{qP}, L_{Pq} and L_{PP} are the transport coefficients, which are four second-order tensors. They should satisfy the generalized Onsager relations [14]
$L_{qq} = L^{T}_{qq}$, $L_{qP} = L^{T}_{Pq}$,

$$\boldsymbol{L}_{PP} = \boldsymbol{L}^{T}_{PP} \tag{35}$$

Because to a first-order ferroelectric phase transition the electric displacement changes suddenly and so does the internal electrical potential, the force X_P of the region where the phase transition is occurring can be regarded as a large constant roughly in the characteristic

times of phase transition (i.e. the times in which the interface keeps rest). For the ferroelectric phase transition may be regarded as a stationary states process, the principle of minimum entropy production must be satisfied [15].

According to Equations (30)-(35), we have

$$\sigma_s = \boldsymbol{L}_{qq} : \boldsymbol{X}_q \boldsymbol{X}_q + 2\boldsymbol{L}_{qP} : \boldsymbol{X}_q \boldsymbol{X}_P + \boldsymbol{L}_{PP} : \boldsymbol{X}_P \boldsymbol{X}_P \tag{36}$$

If there is no any restriction on X_q and X_P, according to the conditions on which the entropy production is a minimum

$$\left(\frac{\partial \sigma_s}{\partial \boldsymbol{X}_q} \right)_{\boldsymbol{X}_P} = 2\boldsymbol{L}_{qq} \cdot \boldsymbol{X}_q + 2\boldsymbol{L}_{qP} \cdot \boldsymbol{X}_P = 2\boldsymbol{J}_q = 0 \tag{37}$$

$$\left(\frac{\partial \sigma_s}{\partial \boldsymbol{X}_P} \right)_{\boldsymbol{X}_q} = 2\boldsymbol{L}_{Pq} \cdot \boldsymbol{X}_q + 2\boldsymbol{L}_{PP} \cdot \boldsymbol{X}_P = 2\boldsymbol{J}_P = 0 \tag{38}$$

We know the stationary states are equilibrium ones actually. If we let X_q (or X_P) be a constant, according to Equation (38) (or (37)) we know J_P (or J_q) which is corresponded to another force X_P (or X_q) should be zero.

Then, a first-order ferroelectric phase transition can be described by the second paradigm. Since the force X_P of the region where the phase transition is occurring is a large constant, the flux J_q of this region should be zero (but $J_P \neq 0$). This states clearly that the pure heat conduction and the heat conduction induced by the thermo-electric coupling cancel out each other so as to release or absorb the latent heat. It is certain that the latent heat passes through the region where the phase transition has occurred (at the outside of the region where the phase transition is occurring) and exchanges itself with the thermal bath. Accompanied with the change of the surface's temperature and the unceasing jerky moving of the region where the phase transition is occurring, a constant temperature gradient is kept in the region where the phase transition has occurred, i.e. the force X_q is a constant. So, the flux $J_P = 0$ (but $J_q \neq 0$). This states clearly that the electric displacement of the region where the phase transition has occurred will not change but keep the value at Curie temperature or zero until the phase transition finishes. Differently, the region where the phase transition will occur should be described by the first paradigm for there is no restriction on the two forces X_P, X_q. The states of this region are equilibrium ones. So the temperature gradient ∇T should be zero.

Considering that $(\nabla T)_{par} \approx 0$ for the region where the phase transition will occur (i.e. the paraelectric phase part) can be regarded as an equilibrium system, we modify Equation (14) as

http://dx.doi.org/10.5772/52089

$$v_n = \frac{k_{fer}\left(\nabla T\right)_{fer} \cdot \boldsymbol{n}}{l\rho} \tag{39}$$

In order to compare it with the experiments, we make use of the following values which are about $PbTiO_3$ crystal: ρ =7.1g/cm^3 [16], l =900cal/mol [17], k_{fer} =8.8 × 10^{5}erg/cmsK [18]. The value of the velocity of the interface's fast motion, which has been measured in the experiments, is 0.5mm/s [11]. According to Equation (39), we calculate the corresponding temperature gradient to be 57.35K/cm. However, in [19] it is reported that the experimental temperature gradient varies from 1.5 to 3.5K/mm while the experimental velocity of the interface's motion varies from 732 to 843μm/s. Considering the model is rather rough, we may conclude that the theory coincides with the experiments.

3.3. Relation between latent heat and spontaneous polarization

In the experiments, the latent heat and the spotaneous polarization are measured often for first-order ferroelectric phase transitions. So in the follows, we will establish the relation between latent heat and spontaneous polarization in the realm of non-equilibrium thermodynamics.

All the quantities of the region where the phase transition has occurred are marked with the superscript "I"; all the quantities of the region where the phase transition is occurring are marked with the superscript "II"; and all the quantities of the region where the phase transition will occur are marked with the superscript "III". Let's consider the heating processes of phase transition firstly. In the region where the phase transition has occurred,

$$\boldsymbol{J}_q^{I-para} = \boldsymbol{L}_{qq}^{I-para} \cdot \boldsymbol{X}_q^{I-para} = l\rho \boldsymbol{v}_a \tag{40}$$

where we have ignored the difference between the mass density of ferroelectric phase and that of paraelectric phase (almost the same) and denote them as ρ, v_a is the average velocity of interface. In the region where the phase transition is occurring,

$$\boldsymbol{J}_q^{II} = \boldsymbol{L}_{qq}^{II} \cdot \boldsymbol{X}_q^{II} + \boldsymbol{L}_{qP}^{II} \cdot \boldsymbol{X}_P^{II} = 0 \tag{41}$$

$$\boldsymbol{J}_P^{II} = \boldsymbol{L}_{Pq}^{II} \cdot \boldsymbol{X}_q^{II} + \boldsymbol{L}_{PP}^{II} \cdot \boldsymbol{X}_P^{II} \tag{42}$$

The heat which is transferred to the region where the phase transition is occurring is absorbed as the latent heat because the pure heat conduction and the heat conduction induced by the thermo-electric coupling cancel out each other. So,

$$l\rho \boldsymbol{v}_a = \boldsymbol{L}_{qq}^{II} \cdot \boldsymbol{X}_q^{II} \tag{43}$$

According to Eqations (41)-(43), we work out

$$\boldsymbol{J}_P^{II} = l\rho \left[\boldsymbol{L}_{Pq}^{II} \cdot \left(\boldsymbol{L}_{qq}^{II} \right)^{-1} - \boldsymbol{L}_{PP}^{II} \cdot \left(\boldsymbol{L}_{qP}^{II} \right)^{-1} \right] \cdot \boldsymbol{v}_a \tag{44}$$

where the superscript "-1" means reverse. While

$$\int \boldsymbol{J}_P^{II} \mathrm{d}t = -\boldsymbol{D}^{spon} = \varepsilon_0 \nabla \varphi_i^{III} - \boldsymbol{P}^{spon-III} = -\boldsymbol{P}^{spon-III} \tag{45}$$

where we utilized the boundary condition of D and considered the region where the phase transition will occur is in equilibrium, the superscript "spon" means spontaneous. So,

$$\boldsymbol{P}^{spon} = \boldsymbol{P}^{spon-III} = -\int \boldsymbol{J}_P^{II} \mathrm{d}t \tag{46}$$

The relation between latent heat and spontaneous polarization are obtained. In the cooling processes of phase transition,

$$-l\rho \boldsymbol{v}_a = \boldsymbol{L}_{qq}^{I-ferr} \cdot \boldsymbol{X}_q^{I-ferr} + \boldsymbol{L}_{qP}^{I-ferr} \cdot \boldsymbol{X}_P^{I-ferr} = \boldsymbol{L}_{qq}^{II} \cdot \boldsymbol{X}_q^{II} \tag{47}$$

$$\int \boldsymbol{J}_P^{II'} \mathrm{d}t = \boldsymbol{D}^{spon-I} = -\varepsilon_0 \nabla \varphi_i^I + \boldsymbol{P}^{spon-I} \tag{48}$$

Repeating the above steps, we obtain

$$\boldsymbol{P}^{spon-I} = \int \boldsymbol{J}_P^{II'} \mathrm{d}t + \varepsilon_0 \nabla \varphi_i^I \tag{49}$$

With

$$\boldsymbol{J}_P^{II'} = -l\rho \left[\boldsymbol{L}_{Pq}^{II} \cdot \left(\boldsymbol{L}_{qq}^{II} \right)^{-1} - \boldsymbol{L}_{PP}^{II} \cdot \left(\boldsymbol{L}_{qP}^{II} \right)^{-1} \right] \cdot \boldsymbol{v}_a = -\boldsymbol{J}_P^{II} \tag{50}$$

Then we find that $P^{spon-III}$ (serves as the equilibrium polarization) is not equal P^{spon-I} (serves as the non-equilibrium polarization). For the region where the phase transition will occur is

stressed [9], there is some difference between $P^{spon}\left(=P^{spon-III}\right)$ and the equilibrium spontaneous polarization without the affects of stress $P^{spon'}$ because of the piezoelectric effect.

4. Thermo-electro-mechanical coupling

The comprehensive thermo-electro-mechanical coupling may be found in ferroelectric phase transition processes. Because there exists not only the change of polarization but also the changes of the system's volume and shape when a ferroelectric phase transition occurs in it, the mechanics can not be ignored even if it is mechanically-free, i.e. no external force is exerted on it. To a first-order ferroelectric phase transition, it occurs at the surface layer of system firstly, then in the inner part. So, the stress may be found in the system.

Since one aspect of the nature of ferroelectric phase transitions is the thermo-electro-mechanical coupling, we take the mechanics into account on the basis of Section 3, where only the thermo-electric coupling has been considered. This may lead to a complete description in the sense of continuum physics.

4.1. Deformation mechanics

For a continuum, the momentum equation in differential form can be written as

$$\nabla \cdot \boldsymbol{\sigma} + \rho \boldsymbol{f} = \rho \boldsymbol{a} \tag{51}$$

where σ, f, a, ρ is the stress, the volume force exerted on unit mass, the acceleration and the mass density, respectively. Let $k = \frac{1}{2}v^2$ be the local kinetic energy density (per unit mass), with v is the velocity. Then

$$\frac{\mathrm{d}k}{\mathrm{d}t} = \boldsymbol{v} \cdot \boldsymbol{a} \tag{52}$$

where t is the time. In terms of

$$\nabla \cdot (v \cdot \sigma) = v \cdot (\nabla \cdot \sigma) + (\nabla v) : \sigma \tag{53}$$

$$\boldsymbol{\sigma} : \left(\nabla \boldsymbol{v}\right) = \boldsymbol{\sigma} : \boldsymbol{d} \tag{54}$$

we can deduce the following balance equation of mechanical energy basing on Equations (51) (52)

$$\rho \frac{\mathrm{d}k}{\mathrm{d}t} - \nabla \cdot (v \cdot \sigma) = \rho v \cdot f - \sigma : d \tag{55}$$

which is in differential form and in Lagrangian form. Or in Eulerian form

$$\frac{\partial(\rho k)}{\partial t} + \nabla \cdot (\rho k v - v \cdot \sigma) = \rho v \cdot f - \sigma : d \tag{56}$$

where $d = \frac{1}{2}(\nabla v + v\nabla) = \frac{1}{2}[\nabla v + (\nabla v)^T]$ is the rate of deformation or strain rate (the superscript "T" means transposition).

To a ferroelectric phase transition, f and σ may be the nominal volume force and stress, which are the embodiments of the actions of thermo-electro-mechanical coupling and are two internal fields. Generally, they are the sums of real and nominal volume force or stress

$$\boldsymbol{f} = \boldsymbol{f}^{real} + \boldsymbol{f}^{nom} \tag{57}$$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{real} + \boldsymbol{\sigma}^{nom} \tag{58}$$

The nominal volume force and stress are not zero until the eigen (or free) deformation of system finishes in phase transitions. If they are zero, the eigen (or free) deformation finishes.

4.2. Local entropy production and description of phase transitions

The Gibbs equation was given as the following [9]

$$T\,\mathrm{d}s + \sum_i \mu_i \mathrm{d}n_i + \frac{1}{\rho} E \cdot \mathrm{d}D + f \cdot \mathrm{d}r + \frac{1}{\rho} \nabla \cdot (v \cdot \sigma)\mathrm{d}t = \mathrm{d}u + \mathrm{d}k \tag{59}$$

where T, E, D is the local temperature, the local electric field intensity and the local electric displacement, respectively; s, u, n_i, μ_i is the local entropy density (per unit mass), the local internal energy density (per unit mass), the local molar quantity density (per unit mass) and the chemical potential, respectively; r is the displacement vector. If the external electric field is not applied, the quantity E is the internal electric field E_i only [8].

Make the material derivative of Equation (59) with t, then obtain

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} + \frac{\rho}{T} \sum_i \mu_i \frac{\mathrm{d}n_i}{\mathrm{d}t} + \frac{1}{T} E_i \cdot \frac{\mathrm{d}D}{\mathrm{d}t} + \frac{\rho}{T} f \cdot \frac{\mathrm{d}r}{\mathrm{d}t} + \frac{1}{T} \nabla \cdot (v \cdot \sigma) = \frac{\rho}{T} \frac{\mathrm{d}e}{\mathrm{d}t} \tag{60}$$

http://dx.doi.org/10.5772/52089

where e is the total energy with $e = u + k$. We know, the system is in the crystalline states before and after a phase transition so that there is no diffusion of any kind of particles in the system. So, n_i as the local molar quantity (per unit mass) does not change with t, i.e. $\frac{dn_i}{dt} = 0$. $\frac{dD}{dt}$ stands for the polarization current J_P, while $\frac{dr}{dt}$ stands for the velocity v, $E_i = -\nabla\varphi_i$ (φ_i stands for the internal electric potential).

After the lengthy and troublesome deduction [9], the local entropy balance equation in Lagrangian form can be obtained

$$\rho\frac{\mathrm{d}s}{\mathrm{d}t} = -\nabla\cdot\boldsymbol{J}_s + \sigma_s \tag{61}$$

with the entropy flux J_s

$$J_s = \frac{J_q^{diff} + \varphi_i J_P - v\cdot\sigma}{T} \tag{62}$$

and the rate of local entropy production σ_s

$$\sigma_s = J_q^{diff}\cdot\nabla\left(\frac{1}{T}\right) + J_P\cdot\nabla\left(\frac{\varphi_i}{T}\right) - \sigma:\left[v\nabla\left(\frac{1}{T}\right)\right] - \rho f\cdot\frac{v}{T} \tag{63}$$

where J_q^{diff} is the diffusion of heat, i.e. heat conduction.

Here are the thermodynamic fluxes $J_q^{diff}\,(=J_q)$, J_P, $\sigma\,(=J_\sigma)$, $\rho f\,(=J_f)$ and the corresponding thermodynamic forces X_q, X_P, X_σ, X_f

$$\boldsymbol{X}_q = \nabla\left(\frac{1}{T}\right) \tag{64}$$

$$\boldsymbol{X}_P = \nabla\left(\frac{\varphi_i}{T}\right) \tag{65}$$

$$\boldsymbol{X}_\sigma = -\boldsymbol{v}\nabla\left(\frac{1}{T}\right) \tag{66}$$

$$\boldsymbol{X}_f = -\frac{\boldsymbol{v}}{T} \tag{67}$$

$J_i(i=q,\ P,\ \sigma,\ f)$ can be expanded linearly with $X_j(j=q,\ P,\ \sigma,\ f)$

$$\boldsymbol{J}_q = \boldsymbol{L}_{qq} \cdot \boldsymbol{X}_q + \boldsymbol{L}_{qP} \cdot \boldsymbol{X}_P + \boldsymbol{L}_{q\sigma} : \boldsymbol{X}_\sigma + \boldsymbol{L}_{qf} \cdot \boldsymbol{X}_f \tag{68}$$

$$\boldsymbol{J}_P = \boldsymbol{L}_{Pq} \cdot \boldsymbol{X}_q + \boldsymbol{L}_{PP} \cdot \boldsymbol{X}_P + \boldsymbol{L}_{P\sigma} : \boldsymbol{X}_\sigma + \boldsymbol{L}_{Pf} \cdot \boldsymbol{X}_f \tag{69}$$

$$\boldsymbol{J}_\sigma = \boldsymbol{L}_{\sigma q} \cdot \boldsymbol{X}_q + \boldsymbol{L}_{\sigma P} \cdot \boldsymbol{X}_P + \boldsymbol{L}_{\sigma\sigma} : \boldsymbol{X}_\sigma + \boldsymbol{L}_{\sigma f} \cdot \boldsymbol{X}_f \tag{70}$$

$$\boldsymbol{J}_f = \boldsymbol{L}_{fq} \cdot \boldsymbol{X}_q + \boldsymbol{L}_{fP} \cdot \boldsymbol{X}_P + \boldsymbol{L}_{f\sigma} : \boldsymbol{X}_\sigma + \boldsymbol{L}_{ff} \cdot \boldsymbol{X}_f \tag{71}$$

where L_{qq}, L_{PP}, L_{ff}, L_{qP}, L_{Pq}, L_{qf}, L_{fq}, L_{Pf}, L_{fP} are nine second-order tensors, $L_{q\sigma}$, $L_{\sigma q}$, $L_{P\sigma}$, $L_{\sigma P}$, $L_{\sigma f}$, $L_{f\sigma}$ are six third-order tensors, $L_{\sigma\sigma}$ is a fourth-order tensor. They should satisfy the generalized Onsager relations [14]
$L_{\alpha\alpha} = L^{T}_{\alpha\alpha}$

$$\left(\alpha = q,\ P,\ \sigma, f\right) \tag{72}$$

$L_{\alpha\beta} = L^{T}_{\beta\alpha}$

$$\left(\alpha,\ \beta = q,\ P,\ \sigma, f,\ \text{and}\ \alpha \neq \beta\right) \tag{73}$$

So the rate of local entropy production can be written as

$$\begin{aligned}
\sigma_s = {} & \boldsymbol{L}_{qq} : \boldsymbol{X}_q \boldsymbol{X}_q + \boldsymbol{L}_{qP} \cdot\cdot \boldsymbol{X}_P \boldsymbol{X}_q + \boldsymbol{L}_{q\sigma} \cdots \boldsymbol{X}_\sigma^T \boldsymbol{X}_q + \boldsymbol{L}_{qf} \cdot\cdot \boldsymbol{X}_f \boldsymbol{X}_q \\
& + \boldsymbol{L}_{Pq} \cdot\cdot \boldsymbol{X}_q \boldsymbol{X}_P + \boldsymbol{L}_{PP} : \boldsymbol{X}_P \boldsymbol{X}_P + \boldsymbol{L}_{P\sigma} \cdots \boldsymbol{X}_\sigma^T \boldsymbol{X}_P + \boldsymbol{L}_{Pf} \cdot\cdot \boldsymbol{X}_f \boldsymbol{X}_P \\
& + \boldsymbol{L}_{\sigma q} \cdots \boldsymbol{X}_q \boldsymbol{X}_\sigma^T + \boldsymbol{L}_{\sigma P} \cdots \boldsymbol{X}_P \boldsymbol{X}_\sigma^T + \boldsymbol{L}_{\sigma\sigma} \cdots\cdot \boldsymbol{X}_\sigma^T \boldsymbol{X}_\sigma^T + \boldsymbol{L}_{\sigma f} \cdots \boldsymbol{X}_f \boldsymbol{X}_\sigma^T \\
& + \boldsymbol{L}_{fq} \cdot\cdot \boldsymbol{X}_q \boldsymbol{X}_f + \boldsymbol{L}_{fP} \cdot\cdot \boldsymbol{X}_P \boldsymbol{X}_f + \boldsymbol{L}_{f\sigma} \cdots \boldsymbol{X}_\sigma^T \boldsymbol{X}_f + \boldsymbol{L}_{ff} : \boldsymbol{X}_f \boldsymbol{X}_f
\end{aligned} \tag{74}$$

According to the condition on which the local entropy production is a minimum, from Equation (74) we can deduce the following

http://dx.doi.org/10.5772/52089

$$\begin{aligned}\left(\frac{\partial \sigma_s}{\partial \boldsymbol{X}_q}\right)_{\boldsymbol{X}_P,\boldsymbol{X}_\sigma,\boldsymbol{X}_f} &= 2\boldsymbol{L}_{qq}\cdot\boldsymbol{X}_q+\boldsymbol{L}_{qP}\cdot\boldsymbol{X}_P+\boldsymbol{L}_{q\sigma}:\boldsymbol{X}_\sigma+\boldsymbol{L}_{qf}\cdot\boldsymbol{X}_f\\ &+\boldsymbol{L}_{Pq}^T\cdot\boldsymbol{X}_P+\boldsymbol{L}_{\sigma q}^T:\boldsymbol{X}_\sigma+\boldsymbol{L}_{fq}^T\cdot\boldsymbol{X}_f\\ &=2\left(\boldsymbol{L}_{qq}\cdot\boldsymbol{X}_q+\boldsymbol{L}_{qP}\cdot\boldsymbol{X}_P+\boldsymbol{L}_{q\sigma}:\boldsymbol{X}_\sigma+\boldsymbol{L}_{qf}\cdot\boldsymbol{X}_f\right)\\ &=2\boldsymbol{J}_q\\ &=0\end{aligned} \tag{75}$$

$$\begin{aligned}\left(\frac{\partial \sigma_s}{\partial \boldsymbol{X}_P}\right)_{\boldsymbol{X}_q,\boldsymbol{X}_\sigma,\boldsymbol{X}_f} &= \boldsymbol{L}_{qP}^T\cdot\boldsymbol{X}_q+\boldsymbol{L}_{Pq}\cdot\boldsymbol{X}_q+2\boldsymbol{L}_{PP}\cdot\boldsymbol{X}_P+\boldsymbol{L}_{P\sigma}:\boldsymbol{X}_\sigma\\ &+\boldsymbol{L}_{Pf}\cdot\boldsymbol{X}_f+\boldsymbol{L}_{\sigma P}^T:\boldsymbol{X}_\sigma+\boldsymbol{L}_{fP}^T\cdot\boldsymbol{X}_f\\ &=2\left(\boldsymbol{L}_{Pq}\cdot\boldsymbol{X}_q+\boldsymbol{L}_{PP}\cdot\boldsymbol{X}_P+\boldsymbol{L}_{P\sigma}:\boldsymbol{X}_\sigma+\boldsymbol{L}_{Pf}\cdot\boldsymbol{X}_f\right)\\ &=2\boldsymbol{J}_P\\ &=0\end{aligned} \tag{76}$$

$$\begin{aligned}\left(\frac{\partial \sigma_s}{\partial \boldsymbol{X}_\sigma}\right)_{\boldsymbol{X}_q,\boldsymbol{X}_P,\boldsymbol{X}_f} &= \boldsymbol{L}_{q\sigma}^T\cdot\boldsymbol{X}_q+\boldsymbol{L}_{P\sigma}^T\cdot\boldsymbol{X}_P+\boldsymbol{L}_{\sigma q}\cdot\boldsymbol{X}_q+\boldsymbol{L}_{\sigma P}\cdot\boldsymbol{X}_P\\ &+2\boldsymbol{L}_{\sigma\sigma}:\boldsymbol{X}_\sigma+\boldsymbol{L}_{\sigma f}\cdot\boldsymbol{X}_f+\boldsymbol{L}_{f\sigma}^T\cdot\boldsymbol{X}_f\\ &=2\left(\boldsymbol{L}_{\sigma q}\cdot\boldsymbol{X}_q+\boldsymbol{L}_{\sigma P}\cdot\boldsymbol{X}_P+\boldsymbol{L}_{\sigma\sigma}:\boldsymbol{X}_\sigma+\boldsymbol{L}_{\sigma f}\cdot\boldsymbol{X}_f\right)\\ &=2\boldsymbol{J}_\sigma\\ &=0\end{aligned} \tag{77}$$

$$\begin{aligned}\left(\frac{\partial \sigma_s}{\partial \boldsymbol{X}_f}\right)_{\boldsymbol{X}_q,\boldsymbol{X}_P,\boldsymbol{X}_\sigma} &= \boldsymbol{L}_{qf}^T\cdot\boldsymbol{X}_q+\boldsymbol{L}_{Pf}^T\cdot\boldsymbol{X}_P+\boldsymbol{L}_{\sigma f}^T:\boldsymbol{X}_\sigma+\boldsymbol{L}_{fq}\cdot\boldsymbol{X}_q\\ &+\boldsymbol{L}_{fP}\cdot\boldsymbol{X}_P+\boldsymbol{L}_{f\sigma}:\boldsymbol{X}_\sigma+2\boldsymbol{L}_{ff}\cdot\boldsymbol{X}_f\\ &=2\left(\boldsymbol{L}_{fq}\cdot\boldsymbol{X}_q+\boldsymbol{L}_{fP}\cdot\boldsymbol{X}_P+\boldsymbol{L}_{f\sigma}:\boldsymbol{X}_\sigma+\boldsymbol{L}_{ff}\cdot\boldsymbol{X}_f\right)\\ &=2\boldsymbol{J}_f\\ &=0\end{aligned} \tag{78}$$

This reveals that if the k forces among those are kept constant, i.e. $X_i=const(i=1, 2, \cdots, k, k<4)$, the fluxes corresponding to the left $4-k$ forces are zero. Of course, if there are no restrictions on $X_i(i=1, 2, 3, 4)$, all the flues are zero. (For convenience, we have modified the superscripts q, P, σ, f to be 1,2,3,4).

We may describe a ferroelectric phase transition by using the two paradigms above similarly as we have done in Section 3. To a first-order ferroelectric phase transition, the forces X_P, X_σ, X_f of the region where the phase transition is occurring can be regarded as three large constants roughly in the characteristic times of phase transition (i.e. the times in which the interface keeps rest) because the electric displacement, the volume and the shape change suddenly. So, the flux J_q^{diff} of the region should be zero (but $J_P \neq 0$, $\sigma \neq 0$, $\rho f \neq 0$). This states clearly that the pure heat conduction and the heat conduction induced by the thermo-electric coupling and the thermo-mechanical coupling cancel out each other so as to release or absorb the latent heat. The phase transition occurs at the surface layer firstly, which is mechanically-free. So, when the phase transition occurs in this region, the flux σ maybe the nominal stress σ^{nom} only, which does work to realize the transformation from internal energy to kinetic energy. When the phase transition occurs in the inner part, the flux σ should be the sum of σ^{real} and σ^{nom} because the sudden changes of the inner part's volume and shape have to overcome the bound of outer part then σ^{real} arises. The region where the phase transition is occurring, i.e. the phase boundary is accompanied with the real stress σ^{real} usually, which does work to realize the transformation from kinetic energy to internal energy. This has been predicted and described with a propagating stress wave [20].

It is certain that the latent heat passes through the region where the phase transition has occurred (at the outside of the region where the phase transition is occurring) and exchange itself with the thermal bath. For $\pm l\rho v_a = J_q^{diff} = -\kappa \cdot \nabla T$, a constant temperature gradient ∇T is kept in the region where the phase transition has occurrd, i.e. the force X_q at every site is a constant (which does not change with the time but may vary with the position). So, the fluxes $J_P = \sigma = \rho f = 0$ (but the flux $J_q^{diff} \neq 0$). This states clearly that the electric displacement D will not change but keep the value at Curie temperature or zero until the phase transition finishes and $\sigma^{real} = -\sigma^{nom}$ in this region. Because the electric displacement D and the strain (or deformation) are all determined by the crystal structure of system, $J_P = 0$ reveals that D of this region does not change so does not the crystal structure then does not the strain (or deformation). According to [20], we know the region where the phase transition has occurred is unstressed, i.e. $\sigma^{real} = 0$, then $\sigma^{nom} = 0$. This reveals that the eigen (or free) strain (or deformation) of system induced by the thermo-electro-mechanical coupling of phase transition is complete and the change of it terminates before the phase transition finishes. The two deductions coincide with each other. σ^{real} may relaxes via the free surface.

The region where the phase transition will occur should be in equilibrium because there are no restrictions on the forces X_q, X_P, X_σ, X_f. Whereas, according to [20], the region is stressed, i.e. $\sigma^{real} \neq 0$. To the heating process of phase transition, this may lead to a change of the spontaneous polarization of this region because of the electro-mechanical coupling (piezo-electric effect).

An immediate result of the above irreversible thermodynamic description is that the action at a distance, which is the kind of heat transfer at phase transitions, is removed absolutely. The

http://dx.doi.org/10.5772/52089

latent heat is transferred within a finite time so the occurrence of phase transition in the inner part is delayed. (Of course, another cause is the stress, just see Section 5) In other words, the various parts absorb or release the latent heat at the various times. The action at a distance does not affect the phase transition necessarily.

5. Irreversibility: Thermal hysteresis and occurrences of domain structure

5.1. Thermal hysteresis

The "thermal hysteresis" of first-order ferroelectric phase transitions is an irreversible phenomenon obviously. But it was treated by using the equilibrium thermodynamics for ferroelectric phase transitions, the well-known Landau-Devonshire theory [2]. So, there is an inherent contradiction in this case. The system in which a first-order ferroelectric phase transition occurs is heterogeneous. The occurrences of phase transition in different parts are not at the same time. The phase transition occurs at the surface layer then in the inner part of system. According to the description above, we know a constant temperature gradient is kept in the region where the phase transition has occurred. The temperature of surface layer, which is usually regarded as the temperature of the whole system in experiments, must be higher (or lower) than the Curie temperature. This may lead to the thermal hysteresis.

No doubt that the shape and the area of surface can greatly affect the above processes. We may conclude that the thermal hysteresis can be reduced if the system has a larger specific surface and, the thermal hysteresis can be neglected if a finite system has an extremely-large specific surface. So, the thermal hysteresis is not an intrinsic property of the system.

The region where the phase transition will occur can be regarded as an equilibrium system for there are no restrictions on the forces X_q, X_P, X_σ, X_f. In other words, the forces and the corresponding fluxes are zero in this region. To a system where a second-order ferroelectric phase transition occurs, the case is somewhat like that of the region where a first-order ferroelectric phase transition will occur. The spontaneous polarization, the volume and the shape of system are continuous at the Curie temperature and change with the infinitesimal magnitudes. This means X_q, X_P, X_σ, X_f and J_q^{diff}, J_P, σ, ρf can be arbitrary infinitesimal magnitudes. The second-order phase transition occurs in every part of the system simultaneously, i.e. there is no the co-existence of two phases (ferroelectric and paraelectric). So, there is no the latent heat and stress. The thermal hysteresis disappears.

The region where a first-order ferroelectric phase transition will occur is stressed. This reveals that the occurrences of phase transition in the inner part have to overcome the bound of outer part, where the phase transition occurs earlier. This may lead to the delay of phase transition in the inner part.

5.2. Occurrences of domain structure

Though the rationalization of the existence of domain structures can be explained by the equilibrium thermodynamics, the evolving characteristics of domain occurrences in

ferroelectrics can not be explained by it, but can be explained by the non-equilibrium thermodynamics.

In the region where the phase transition is occurring, the thermodynamic forces X_P $(= \nabla\left(\frac{\varphi_i}{T}\right))$, X_σ $(= -v\nabla\left(\frac{1}{T}\right))$, X_f $(= -\frac{v}{T})$ can be regarded as three large constants in the characteristic times of transition and the thermodynamic flux $J_q^{diff} = 0$ (but $J_P \neq 0$, $\sigma \neq 0$, $\rho f \neq 0$). The local entropy production (cf. Equation (63)) reduces to

$$\sigma_s = \boldsymbol{J_P} \cdot \nabla\left(\frac{\varphi_i}{T}\right) - \quad : \left[\boldsymbol{v}\nabla\left(\frac{1}{T}\right)\right] - \rho \boldsymbol{f} \cdot \frac{\boldsymbol{v}}{T} \tag{79}$$

Now, we are facing a set of complicated fields of T, v and φ_i, respectively. Assume that the phase transition front is denoted by S. The points included in S stand for the locations where the transition is occurring. Because the transition occurs along all directions from the outer part to the inner part, we may infer that the orientations of $\nabla\left(\frac{\varphi_i}{T}\right)$, or of $-v\nabla\left(\frac{1}{T}\right)$ and or of $-\frac{v}{T}$ vary continuously such that they are differently oriented at different locations.

There are always several (at least two) symmetry equivalent orientations in the prototype phase (in most cases it is the high temperature phase), which are the possible orientations for spontaneous polarization (or spontaneous deformation or spontaneous displacement). Therefore, the spontaneous polarization, the spontaneous deformation and the spontaneous displacement must take an appropriate orientation respectively to ensure σ_s is a positive minimum when the system transforms from the prototype (paraelectric) phase to the ferroelectric (low temperature) phase. The underlying reasons are that

$$\boldsymbol{J_P} = \frac{\mathrm{d}\boldsymbol{D}}{\mathrm{d}t} = \frac{\mathrm{d}\left(\varepsilon_0 \boldsymbol{E_i} + \boldsymbol{P}\right)}{\mathrm{d}t} \tag{80}$$

$$= \boldsymbol{L} : \boldsymbol{\varepsilon} \tag{81}$$

$$\rho \boldsymbol{f} = \rho \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} - \nabla \cdot \tag{82}$$

where L , ε, and ε_0 are the modulus of rigidity, the strain and the permittivity of vacuum, respectively. Therefore, P, ε at different locations will be differently oriented. The domain structures in ferroelectrics thus occur.

http://dx.doi.org/10.5772/52089

It seems that the picture of domain occurrences for first-order ferroelectric phase transition systems should disappear when we face second-order ferroelectric phase transition systems. This is true if the transition processes proceed infinitely slowly as expounded by the equilibrium thermodynamics. But any actual process proceeds with finite rate, so it is irreversible. Then the above picture revives.

In [21], the domain occurrences in ferromagnetics can be described parallelly by analogy. And the case of ferroelastic domain occurrences is a reduced, simpler one compared with that of ferroelectrics or ferromagnetics.

It is well known that the Landau theory or the Curie principle tells us how to determine the symmetry change at a phase transition. A concise statement is as follows [22]: for a crystal undergoing a phase transition with a space-group symmetry reduction from G_0 to G, whereas G determines the symmetry of transition parameter (or vice versa), it is the symmetry operations lost in going from G_0 to G that determine the domain structure in the low-symmetry phase. The ferroic phase transitions are the ones accompanied by a change of point group symmetry [23]. Therefore, the substitution of "point group" for the "space group" in the above statement will be adequate for ferroic phase transitions. From the above statement, the domain structure is a manifestation of the symmetry operations lost at the phase transition. In our treatment of the domain occurrences in ferroics, we took into account the finiteness of system (i.e. existence of surface) and the irreversibility of process (asymmetry of time). The finiteness of system make the thermodynamic forces such as $\nabla\left(\frac{\varphi_i}{T}\right)$, $-v\nabla\left(\frac{1}{T}\right)$, $-\frac{v}{T}$ have infinite space symmetry. The infinite space symmetry, combined with the asymmetry of time, reproduces the symmetry operations lost at the phase transition in the ferroic phase. It can be viewed as an embodiment of time-space symmetry.

After all, for the domain structures can exist in equilibrium systems, they are the equilibrium structures but not the dissipative ones, for the latter can only exist in systems far from equilibrium [24].

6. Concluding remarks

In order to overcome the shortcoming of Landau-Devonshire theory, the non-equilibrium thermodynamics was applied to study the ferroelectric phase transitions. The essence of transitions is the thermo-electro-mechanical coupling. Moreover, the irreversibility, namely thermal hysteresis and domain occurrences can be explained well in the realm of non-equilibrium thermodynamics.

The non-equilibrium thermodynamic approach utilized here is the linear thermodynamic one actully. In order to get the more adequate approaches, we should pay attention to the new developments of non-equilibrium thermodynamics. The thermodynamics with internal variables [25] and the extended (irreversible) thermodynamics [26] are two current ones. They all expand the fundamental variables spaces to describe the irreversible processes more

adequately. Whereas, the relevant theoretical processing must be more complicated undoubtly. This situation needs very much effort.

Acknowledgements

The work is supported by the Natural Science Foundation Program of Shandong Province, China (Grant No. ZR2011AM019).

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