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Polar elastic dielectric of large electrocaloric effect and deformation

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ABSTRACT

The alternation of temperature and entropy induced by an electric field in a polar dielectric material is known as the electrocaloric effect (ECE). This paper develops a thermodynamic theory of the polar elastic dielectric with large ECE and large deformation compatibility. The theory characterizes the equilibrium condition of the polar elastic dielectric which is subjected to mechanical forces, electric field and thermal field. The mechanical behavior and large deformation of the polar elastic dielectric thermo-electro-mechanical system are analyzed under the coupling influence of hyperelastic, polarization, electrostriction and thermal contribution on the system. The typical thermodynamics cycles of the polar elastic dielectric are described as cooling devices and generators and the electrocaloric and pyroelectric energy conversion are calculated. Ferroelectric polymer, as an important category of electroactive polymers, is a typical polar dielectric with a large ECE and a large deformation. As an example, when subjected to different voltage, the ferroelectric polymers are regarded as cooling devices. We calculated their temperature change, entropy change, heat absorptions and work generation. We also calculated the voltage change, electric quantity change and work of the ferroelectric polymer which is regarded as generators when subjected to different temperatures. Finally, we investigated the thermo-electro-mechanical coupling behavior of the ferroelectric polymers undergoing ferroelectric–paraelectric phase transition.

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1. Introduction

Polar dielectrics may possess large pyroelectric effect (PCE) and large electrocaloric effect (ECE) (Neese et al., 2008; Lu and Zhang, 2009). After applying a thermal field to the polar dielectric, we could observe an alternation in the polarization and consequently leading to the change of the electric charge (under a constant voltage) or the voltage (under a constant charge). This phenomenon is known as the PCE. On the other hand, the electric field induced change of the entropy (under isothermal conditions) and the temperature (under adiabatic conditions) is named as the ECE (Scott, 2007; Mischenko et al., 2006a). PCE and ECE are mutually reversible in practical applications. The former can be used to design and manufacture generators while the later is frequently explored in cooling devices.

Although ECE has been studied for decades and described in various materials, such as $BaTiO_3$, $KTaO_3$, KH_2PO_4, triglycine sulfate (TGS), $P_b(ZrTi)O_3$, $Pb(ScTa)O_3$, and $SrTiO_3$, the relatively small ECE made it unsuitable for practical applications (Lu and Zhang, 2009; Liu et al., 2010, 2012). Recent findings of large ECE in several

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ferroelectric materials revived the research interest in their applications of dielectric cooling devices (Mischenko et al., 2006b; Neese et al., 2009; Li et al., 2010; Kar-Narayan and Mathur, 2010;Qiu and Jiang, 2009). The manufacture, performance test and application of materials within large ECE are consequently widely investigated (Lu et al., 2010a,b, 2011; Pirc et al., 2011).

Recent experimental results show that antiferroelectric ceramic ($PbZr_{0.95}Ti_{0.05}O_3$) (Lu and Zhang, 2009), normal ferroelectric polymers (poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)]) (Neese et al., 2008), relaxor ferroelectric polymers poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) P(VDF–TrFE–CFE) (Neese et al., 2008), organic and inorganic relaxor ferroelectrics (high energy electron irradiated poly(vinylidene fluoride–trifluoroethylene) relaxor copolymer in the La-doped $Pb(ZrTi)O_3$ relaxor ceramic thin films (Lu et al., 2010a) have large ECE when the temperature range is above a ferroelectric (polarization-ordered)–paraelectric (polarization-disordered) (F–P) phase transition (Neese et al., 2008;Lu and Zhang, 2009; Scott, 2007; Mischenko et al., 2006b; Neese et al., 2009; Li et al., 2010; Kar-Narayan and Mathur, 2010; Qiu and Jiang, 2009; Lu et al., 2010a,b, 2011; Pirc et al., 2011). Mischenko et al. demonstrated a large ECE in antiferroelectric ceramic $PbZr_{0.95}Ti_{0.05}O_3$ above the F–P phase transition (ferroelectric Curie temperature 222 °C), where the electric field is 48 MV/m and the temperature is 230 °C. An adiabatic temperature change of more than 12 °C and isothermal entropy change of more than 8 J/(kg K) were observed (Mischenko et al., 2006a). Zhang et al. fabricated the ferroelectric poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)] 55/45 mol% copolymer at temperatures above the ferroelectric–paraelectric phase transition, when the electric field is 209 MV/m and the temperature is 80 °C. An isothermal entropy change of more than 55 J/(kg K) and adiabatic temperature change of more than 12 K were observed (Neese et al., 2008). Recently, Lu et al. investigated the electrocaloric effect of inorganic thin film and organic relaxor ferroelectrics (Lu et al., 2010a). The results revealed that giant ECEs can be obtained in the high energy electron irradiated poly(vinylidene fluoride–trifluoroethylene) relaxor copolymer and in the La-doped $Pb(ZrTi)O_3$ relaxor ceramic thin films, which are much larger than that from the normal ferroelectric counterparts. Lu et al. reported the directly measured ECE of relaxor ferroelectric poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) terpolymer and its blend with poly(vinylidene fluoride–chlorotrifluoroethylene). An adiabatic temperature change of 12 °C and isothermal entropy change of 55 J/(kg K) have been demonstrated for the terpolymer blend films with 5 wt.% of P(VDF–CTFE) under 170 MV/m and ambient condition (Lu et al., 2010b). Lu et al. also measured the ECE of the ferroelectric poly(vinylidene–fluoride/trifluoroethylene) 55/45 mol% copolymer over a broad temperature range using a specially designed calorimetry method. The data revealed that a large ECE occurring at the ferroelectric–paraelectric (FE–PE) phase transition where the adiabatic temperature change was 12 K, under the electrical field of 120 MV/m, which is much higher than that previously observed at above the FE–PE transition (Lu et al., 2011).

However, the theoretical studies of electrocaloric effect in ferroelectric polymer are relatively rare, most of which are based on the Maxwell relation and calculate the adiabatic temperature change and isothermal entropy change of ferroelectric polymers subjected to diverse electric field (Neese et al., 2008, 2009; Lu and Zhang, 2009). Pirc et al. used thermodynamic and statistical mechanics arguments and derived physical upper bounds on the electrocaloric effect in bulk polar solids (Pirc et al., 2011). Liu et al. modeled polar dielectric based on cooling devices as a system of two degrees of freedom, represented by either the entropy–temperature plane or the electric displacement–electric field plane. Typical thermodynamic energy cyclic path in polar dielectric as cooling devices is proposed. By considering the influence of temperature, the free energy of the thermal–electrical coupling system of polar dielectrics is formulated, and the variation of temperature, entropy, the absorption of heat and the work under different electric field are calculated for several typical polar dielectrics. The simulation results fit well with the recently published experimental data (Liu et al., 2011a).

Electroactive polymers are a category of smart soft materials, which can change their shapes or volumes when subjected to electric fields and can recover the original shapes and volumes when the electric fields are removed (Wissler and Mazza, 2007; Suo et al., 2008; Suo, 2010 Hong, 2011). As a kind of electroactive polymers, ferroelectric polymer could generate large deformation when subjected to electric field, and hence is worthy for our research attentions.

This paper develops a thermodynamic theory of polar dielectrics within large ECE and deformation. The theory characterizes the equilibrium condition of the polar dielectric subjected to mechanical forces, electric field and thermal field. We consider the coupling influence of hyper elastic, polarization, electrostriction and heat contribution to the polar dielectric subject to mechanical forces, electric and thermal fields, and investigate the mechanical behavior and large deformation of the system. The typical thermodynamics cycles of polar dielectric as cooling devices and energy generator are described. The energy transformation between electricity and heat is also calculated. Ferroelectric polymer, as an important category of electroactive polymers, is a typical polar dielectric featuring large ECE and deformation. As an example, we calculated the temperature change, entropy change, absorption of heat and the work of the ferroelectric polymer as cooling devices after different voltage is subjected. We also calculated the voltage change, electric quantity change and work of ferroelectric polymer as energy generator when subjected to different temperatures. Finally, we investigated the mechanical behavior of polar dielectric of large electrocaloric effect and deformation undergoing ferroelectric–paraelectric phase transition.

2. Polar elastic dielectric in equilibrium with an electric field, a thermal field and a set of forces

Fig. 1 illustrates a block of polar-elastic dielectric with large electrocaloric effect and deformation. As shown in

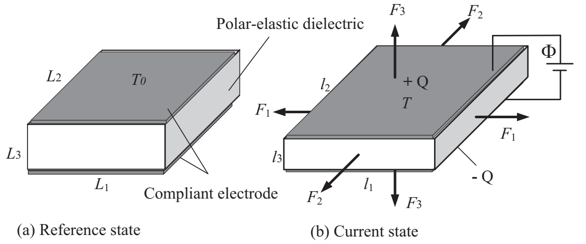


Fig. 1. A block of a polar-elastic dielectric sandwiched between two compliant electrodes. (a) In the reference state, the polar-elastic dielectric is subjected to neither forces nor voltage. (b) In the current state, the dielectric is subjected to forces and voltage, the membrane deforms and charge flows from one electrode to the other through the external conducting wire (Liu et al., 2012).

Fig. 1, we consider a membrane of polar-elastic dielectric sandwiched between compliant homogeneous electrodes. In the reference state, the polar-elastic dielectric is subjected to zero mechanical force and voltage at the temperature T_0, with sides of L_1, L_2 and L_3.

In the current state, the polar-elastic dielectric is subjected to mechanical forces F_1, F_2 and F_3 on three principal directions and voltage U. Heat source of temperature T is also applied at the same time.

Under the coupling effect of mechanical forces, thermal and electrical fields, the polar-elastic dielectric turns into a state of sides l_1, l_2 and l_3 The electric quantity of compliant electrodes on the surfaces are $+Q$, $-Q$, while the entropy is S.

In the current state, the Helmholtz free energy of polar-elastic dielectric thermodynamics system is denoted as H. As the dimension of the polar-elastic dielectric changed by $\delta l_1, \delta l_2$ and δl_3, respectively, the work done by the forces is $F_1\delta l_1 + F_2\delta l_2 + F_3\delta l_3$. Meanwhile, the work done by the voltage is $U\delta Q$ assuming that charges in amount of δQ flows through the thin film. Supposing that there is little temperature change δT in the polar-elastic dielectric, the work done by heat source is $S\delta T$.

That is, the applied mechanical forces are work-conjugate to the displacements, voltage is work-conjugate to the electric charge, and the entropy is work-conjugate to the temperature.

Under the coupling effect of mechanical force, electric field force and heat source, when the polar-elastic dielectric reaches the equilibrium state, the Helmholtz free energy change is equal to the work done by mechanical force, electric field force and heat source. That is

$$\delta H = F_1\delta l_1 + F_2\delta l_2 + F_3\delta l_3 + U\delta Q - S\delta T \tag{1}$$

The condition of equilibrium (1) holds for arbitrary and independent small variations of the five independent quantities l_1, l_2, l_3, Q and T.

We define the stretch of polar-elastic dielectric in the three principal directions are $\lambda_1 = l_1/L_1$, $\lambda_2 = l_2/L_2$, and $\lambda_3 = l_3/L_3$, while the nominal stress are respectively, $\sigma_1^{\sim} = F_1/(l_2 l_3)$, $\sigma_2^{\sim} = F_2/(l_1 l_3)$, and $\sigma_3^{\sim} = F_2/(l_1 l_2)$. Define that the nominal electric field of polar-elastic dielectric is the voltage divided by the undeformed dimensions in the reference state $E^{\sim} = U/L_3$, the nominal electric displacement is the electric quantity divided by the area of dielectric elastomer in the undeformed state $D^{\sim} = Q/(L_1L_2)$, and the nominal topo-entropy density is the electric quantity divided by the volume on the undeformed state $s^{\sim} = S/(L_1L_2L_3)$. The corresponding true stress in three principal directions are respectively $\sigma_1 = F_1/(\lambda_2\lambda_3L_2L_3)$, $\sigma_2 = F_2/(\lambda_1\lambda_3L_1L_3)$ and $\sigma_3 = F_3/(\lambda_1\lambda_2L_1L_2)$. The true electric field is $E = U/(\lambda_3L_3)$, the true electric displacement is $D = Q/(\lambda_1\lambda_2L_1L_2)$, and the true topo-entropy density is $s = S/(l_1l_2l_3)$.

We also define the nominal density of the Helmholtz free energy as $\delta W = \delta H/L_1L_2L_3$.

The condition of equilibrium (1) holds in any current state. Based on the above definitions, we divide Eq. (1) by $L_1L_2L_3$ on the both sides. The small change of the Helmholtz free energy density is expressed as:

$$\delta W = \sigma_1^{\sim}\delta\lambda_1 + \sigma_2^{\sim}\delta\lambda_2 + \sigma_3^{\sim}\delta\lambda_3 + E^{\sim}\delta D^{\sim} - s^{\sim}\delta T \tag{2}$$

This equilibrium condition will hold for arbitrary small variations of the five independent variables, $\lambda_1, \lambda_2, \lambda_3, D^{\sim}$ and T. Considering the influence of temperature, as a material model of the thermo-electro-mechanical coupling thermodynamics system of polar-elastic dielectric, the nominal density of the free energy is taken to be a function of five independent variables:

$$W = W(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T) \tag{3}$$

Under the coupling effect of mechanical force, electric field and heat source, the free energy variation of the thermo-electro-mechanical coupling system of the polar-elastic dielectric can be described as

$$\begin{aligned}\delta W = {} & \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial\lambda_1}\delta\lambda_1 \\ & + \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial\lambda_2}\delta\lambda_2 \\ & + \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial\lambda_3}\delta\lambda_3 \\ & + \frac{\partial(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial D^{\sim}}\delta D^{\sim} + \frac{\partial(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial T}\delta T\end{aligned} \tag{4}$$

Comparing Eq. (2) with (4), we have

$$\begin{aligned}& \left[\frac{\partial W(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial\lambda_1} - \sigma_1^{\sim}\right]\delta\lambda_1 \\ & + \left[\frac{\partial W(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial\lambda_2} - \sigma_2^{\sim}\right]\delta\lambda_2 \\ & + \left[\frac{\partial W(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial\lambda_3} - \sigma_3^{\sim}\right]\delta\lambda_3 \\ & + \left[\frac{\partial(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial D^{\sim}} - E^{\sim}\right]\delta D^{\sim} \\ & + \left[\frac{\partial(\lambda_1, \lambda_2, \lambda_3, D^{\sim}, T)}{\partial T} - s^{\sim}\right]\delta T = 0\end{aligned} \tag{5}$$

This condition of equilibrium holds for any small variations of the five independent variables. Consequently, when the polar-elastic dielectric is in equilibrium with the applied forces, the applied voltage and heat source, the coefficient in front of the variation of each independent variable vanishes.

For arbitrary independent variables $\delta\lambda_1, \delta\lambda_2, \delta\lambda_3, \delta D^{\sim}$ and δT, we have Eq. (5). Therefore, the nominal stress, nominal electric field and nominal topo-entropy density of polar-elastic dielectric are:

$$\sigma_1^{\sim} = \frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\partial \lambda_1} \tag{6}$$

$$\sigma_2^{\sim} = \frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\partial \lambda_2} \tag{7}$$

$$\sigma_3^{\sim} = \frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\partial \lambda_3} \tag{8}$$

$$E^{\sim} = \frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\partial D^{\sim}} \tag{9}$$

$$s^{\sim} = -\frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\partial T} \tag{10}$$

According to the definition above, the true stress, true electric field and true topo-entropy density of the polar-elastic dielectric are written as:

$$\sigma_1 = \frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\lambda_2\lambda_3\partial \lambda_1} \tag{11}$$

$$\sigma_2 = \frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\lambda_1\lambda_3\partial \lambda_2} \tag{12}$$

$$\sigma_3 = \frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\lambda_1\lambda_2\partial \lambda_3} \tag{13}$$

$$E = \frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\lambda_3\partial D^{\sim}} \tag{14}$$

$$s = -\frac{\partial W(\lambda_1,\lambda_2,\lambda_3,D^{\sim},T)}{\lambda_1\lambda_2\lambda_3\partial T} \tag{15}$$

The free energy of the polar elastic dielectric contains four parts, namely the stretching, the electrostriction, the polarization and the thermal contribution. Therefore, the free energy can be described as

$$\begin{aligned} W(\lambda_1,\lambda_2,\lambda_3,T,D^{\sim}) &= U(\lambda_1,\lambda_2,\lambda_3,T) \\ &\quad + V(\lambda_1,\lambda_2,\lambda_3,T,D^{\sim}) + M(T) \end{aligned} \tag{16}$$

where $U(\lambda_1,\lambda_2,\lambda_3,T)$ represents the elastic strain energy of the polar-elastic dielectric, $V(\lambda_1,\lambda_2,\lambda_3,T,D^{\sim})$ represents the electric field energy and $M(T)$ represents the thermal contribution. When specific elastic strain energy, thermal contribution and electric field are provided, according to Eqs. (6)–(15), the equilibrium equation of the thermodynamics system of the polar-elastic dielectric can be determined.

3. Polar dielectric of large PCE and deformation

A dielectric is an electrical insulator that may be polarized by an applied electric field. As shown in Fig. 2, in a polar-elastic dielectric, each polymer chain may consist of monomers of electric dipoles. In the absence of the applied voltage, the dipoles undergo thermal fluctuation, and are randomly oriented, which is similar to water molecules. When the dielectric is subjected to a voltage, the dipoles rotate toward the direction of the electric field. When the voltage becomes sufficiently high, the dipoles become perfectly aligned with the electric field, and the polarization of the material saturate.

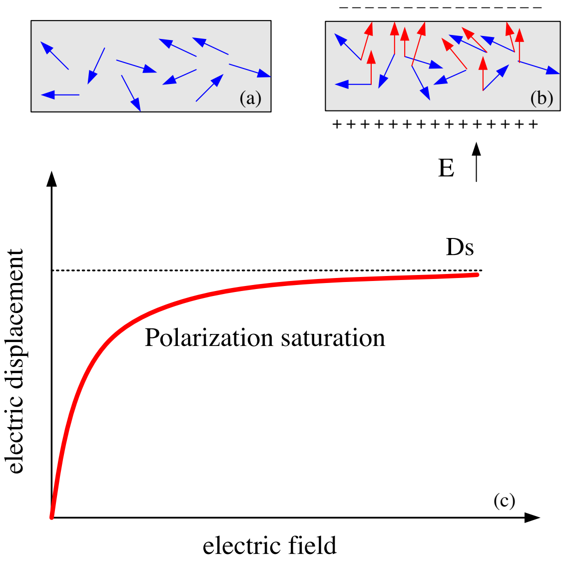


Fig. 2. Dielectric liquid contains (a) lots of molecular dipoles. (b) The polarization is a result of dipole rotation under an electric field, often interpreted as linear, and (c) polarization saturation is obtained when all dipoles are perfectly aligned, when the voltage is high enough as displayed in (d) the overall polarization curve (Liu et al., 2012).

Therefore, when the molecular dipole in the material transforms from the dipole disordered state to ordered state, an entropy change (under isothermal conditions) and temperature (under adiabatic conditions) change will be induced in the change of dipolar states. If the temperature change and the entropy change are large enough in concern, we call that the material possesses large ECE.

Actually, when applied to high electric field, the polar elastic dielectric will generate huge deformation of about 100% (according to the report recently, the deformation can reach 380% maximum), then the chain of molecule would change from the curve state to the unbend state (Zhao and Suo, 2007, 2008; Liu et al., 2011b, 2009). The possible configuration of the material would reduce. That is to say the entropy is diminished, within the entropy change and the temperature change.

Therefore, the temperature change and entropy change of polar elastic dielectric subjected to electric field are depended on two factors, the electrocaloric effect and deformation. Ferroelectric polymer is a kind of typical polar elastic dielectric. When subjected to electric field, large deformation and large ECE will be induced.

4. Incompressible polar elastic dielectric

When an elastomer undergoes large deformation, the change in the shape of the elastomer is typically much larger than the change in the volume. Therefore, the elastomer is often taken to be incompressible. That is, the volume of the material remains unchanged during deformation, $L_1L_2L_3 = l_1l_2l_3$. Then we have

$$\lambda_1\lambda_2\lambda_3 = 1 \tag{17}$$

This assumption of incompressibility places a constraint among the three stretches. Selecting λ_1 and λ_2 as independent variables, we can rewrite Eq. (17) as $\lambda_3 = 1/(\lambda_1\lambda_2)$, and express $\delta\lambda_3$ in terms of $\delta\lambda_1$ and $\delta\lambda_2$

$$\delta\lambda_3 = -\lambda_1^{-2}\lambda_2^{-1}\delta\lambda_1 - \lambda_1^{-1}\lambda_2^{-2}\delta\lambda_2 \tag{18}$$

In terms of the variations of the independent variables, inserting it into Eq. (2), we have

$$\begin{aligned}\delta W = {} & (\sigma_1^{\sim} - \lambda_1^{-2}\lambda_2^{-1}\sigma_3^{\sim})\delta\lambda_1 + (\sigma_2^{\sim} - \lambda_1^{-1}\lambda_2^{-2}\sigma_3^{\sim})\delta\lambda_2 \\ & + E^{\sim}\delta D^{\sim} + s^{\sim}\delta T\end{aligned} \tag{19}$$

The nominal stress in the two planar principal directions, the nominal electric field in the thickness direction, and the nominal local entropy of incompressible elastic dielectric's thermodynamic system are obtained respectively, as is shown in the followings

$$\sigma_1^{\sim} - \frac{\sigma_3^{\sim}}{\lambda_1^2\lambda_2} = \frac{\partial U(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)}{\partial\lambda_1} + \frac{\partial V(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, D^{\sim}, T)}{\partial\lambda_1} \tag{20}$$

$$\sigma_2^{\sim} - \frac{\sigma_3^{\sim}}{\lambda_1\lambda_2^2} = \frac{\partial U(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)}{\partial\lambda_2} + \frac{\partial V(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, D^{\sim}, T)}{\partial\lambda_2} \tag{21}$$

$$E^{\sim} = \frac{\partial V(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, D^{\sim}, T)}{\partial D^{\sim}} \tag{22}$$

$$\begin{aligned}s^{\sim} = {} & -\frac{\partial U(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)}{\partial T} - \frac{\partial V(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, D^{\sim}, T)}{\partial T} \\ & - \frac{\partial M(T)}{\partial T}\end{aligned} \tag{23}$$

And the true stress, the true electric filed and the true local entropy can be expressed as followings

$$\sigma_1 - \sigma_3 = \lambda_1\frac{\partial U(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)}{\partial\lambda_1} + \lambda_1\frac{\partial V(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, D^{\sim}, T)}{\partial\lambda_1} \tag{24}$$

$$\sigma_2 - \sigma_3 = \lambda_2\frac{\partial U(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)}{\partial\lambda_2} + \lambda_2\frac{\partial V(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, D^{\sim}, T)}{\partial\lambda_2} \tag{25}$$

$$E = \lambda_1\lambda_2\frac{\partial V(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, D^{\sim}, T)}{\partial D^{\sim}} \tag{26}$$

$$\begin{aligned}s = {} & -\frac{\partial U(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)}{\partial T} - \frac{\partial V(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, D^{\sim}, T)}{\partial T} \\ & - \frac{\partial M(T)}{\partial T}\end{aligned} \tag{27}$$

Eqs. (20)–(27) constitute the equations of state of incompressible polar-elastic dielectric with large electrocaloric effect and deformation.

5. special free energy, constitutive law, and incompressibility

5.1. A special free energy

Similar with the dielectric elastomer, the ferroelectric polymer is a kind of electronic type electroactive polymers. Polar dielectric having large PCE represented by ferroelectric polymer will induce large electric deformation when subjected to electric field.

The free energy due to the stretching of a network of ferroelectric polymers polar dielectric is taken to be (Liu et al., 2011b)

$$U(\lambda_1, \lambda_2, \lambda_3, T) = \frac{1}{2}NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{28}$$

where N is the number of molecules of the gas in the bubble, and kT is the temperature in the unit of energy. This free energy assumes that contractility of the network is entirely due to the reduction in the entropy caused by stretching the polymer chains, and the configurations of the polymer chains obey the Gaussian statistics. The elastic behavior of the elastomer is neo-Hookean, $\mu = NkT$, where μ is the small strain shear modulus. This free energy is due to the change of entropy when polymer chains are stretched.

For the ferroelectric ceramics represented by $BaTiO_3$, $KTaO_3$, or the antiferroelectric ceramics represented by PZT, the dielectric constant $\varepsilon(T)$ is the function of temperature on paraelectric state, which can be described as (Neese et al., 2008; Lu and Zhang, 2009)

$$\varepsilon(T) = \frac{1}{\alpha(T - T_C)} \tag{29}$$

where $\varepsilon(T)$ is the permittivity of polar dielectric material, α is the phenomenological parameters, and T_C is the Curie temperature.

The theoretical and experimental research of permittivity in soft active dielectric material provided us the idea to analyze the dielectric behavior of polar elastic dielectric. If the crosslinking degree is low and the deformation is well below the extension limit, the molecular units in the polymers can be polarized as freely as those in a polymeric liquid. In this case the corresponding permittivity is unaffected by the deformation. For the condition of dielectric elastomer within small deformation, we can refer to Suo (2010).

The stretching can guide the macromolecule to be arranged in order, and subsequently increases the intermolecular forces and reduce the activities of polar group. As a result, the permittivity will decrease. For the condition of dielectric elastomer within large deformation, we can refer to Zhao and Suo (2008). In addition, the experimental research has indicated that the permittivity of dielectric elastomer is influenced by stretching, as referred in Wissler and Mazza (2007).

Considering the polar dielectric polymers undergoing large deformation and the effect of electrostriction, the linear dielectric constant $\varepsilon(\lambda_1, \lambda_2, \lambda_3, T)$ can be described as (Zhao and Suo, 2008; Liu et al., 2011b)

$$\varepsilon(\lambda_1,\lambda_2,\lambda_3,T)=\varepsilon(T)[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)] \tag{30}$$

Here $\varepsilon(\lambda_1,\lambda_2,\lambda_3,T)$ is the dielectric constant of polar dielectric polymers undergoing temperature change and large deformation. $\varepsilon(T)$ represents the dielectric constant without large deformation. a and b are the electrostriction factors of polar dielectric polymers. And $\lambda_1,\lambda_2,\lambda_3$ are the stretching rate on the direction of plane and thickness of the polar dielectric.

We can get some idea from the study of dielectric elastomer previously (Suo, 2010). For an ideal dielectric elastomer (assuming that the dielectric behavior of an elastomer is exactly the same as that of a polymer melt), the electric field energy per unit volume is $\frac{D^2}{2\varepsilon}$, and the dielectric constant ϵ is a constant independent of deformation (Suo, 2010). The electric field energy per unit volume of incompressible ideal dielectric elastomer is $\frac{\tilde{D}^2}{2\varepsilon}\lambda_1^{-2}\lambda_2^{-2}$ (indicated by nominal dielectric displacement). Considering the electrostriction of dielectric elastomers, the dielectric constant is a function of the stretches, and the electric field energy per unit volume is $\frac{\tilde{D}^2}{2\varepsilon(\lambda_1,\lambda_2,\lambda_3)}\lambda_1^{-1}\lambda_2^{-1}\lambda_3$ (Suo, 2010). The electric field energy per unit volume of incompressible dielectric elastomer within large deformation is $\frac{\tilde{D}^2}{2\varepsilon(\lambda_1,\lambda_2,\lambda_3)}\lambda_1^{-2}\lambda_2^{-2}$.

Considering function (29) and (30), we can get the density function of electric field energy coupling temperature and large deformation as follows

$$V(\lambda_1,\lambda_2,\lambda_3,T,\tilde{D})=\frac{\lambda_1^{-1}\lambda_2^{-1}\lambda_3}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]}\alpha(T-T_C)\tilde{D}^2 \tag{31}$$

We involve the contribution of temperature to the free energy, where the thermal contribution can be expressed as $M(T)=Q(T)-TS$, and here $Q(T)$ is the internal energy (Horgan and Saccomandi, 2006; Wegner and Haddow, 2009; Holzapfel, 2000; Liu et al., 2011a). When the temperature rises, the internal energy changes by $c(T-T_0)$. According to the relation of the heat at constant volume and entropy, $c=T\frac{\partial S}{\partial T}$, we obtain $S=c\log(T/T_0)$. Here, c is the specific heat of polar dielectric. T_0 is the temperature in reference state. T is the temperature in current state.

$$M(T)=c[(T-T_0)-T\log(T/T_0)] \tag{32}$$

Combine Eqs. (24), (27) and (28), we can obtain the specific free energy of the polar dielectric polymers undergoing large deformation and electrocaloric effect as follows

$$\begin{aligned}W(\lambda_1,\lambda_2,\lambda_3,T,\tilde{D})=&\frac{1}{2}NkT(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)\\&+\frac{\lambda_1^{-1}\lambda_2^{-1}\lambda_3}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]}\\&\alpha(T-T_C)\tilde{D}^2+c[(T-T_0)-T\log(T/T_0)]\end{aligned} \tag{33}$$

In Eq. (33), the first item describes the influence of large deformation and temperature, while the second item describes the influence of large deformation, temperature and electric field, and the third item describes the influence of temperature.

Actually, we can choose other elastic strain energy to replace the first item of Eq. (33). For example, we can consider the Mooney–Rivlin elastic strain energy model with two material constants,

$$\begin{aligned}U(\lambda_1,\lambda_2,\lambda_3,T)=&\frac{NkT}{2}[C_1(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)\\&+C_2(\lambda_1^{-2}+\lambda_2^{-2}+\lambda_3^{-2}-3)]\end{aligned}$$

We can also consider the model of elastomer undergoing strain hardening, the Gent elastic strain energy model and Arruda–Boyce elastic strain energy model. Now we introduce the Gent model briefly,

$$U(\lambda_1,\lambda_2,\lambda_3,T)=-\frac{NkT}{2}J_{\lim}\log\left(1-\frac{\lambda_1^2+\lambda_2^2+\lambda_3^2-3}{J_{\lim}}\right)$$

where $J_{\lim}$ is a constant related to the limiting stretch, $J_{\lim}=\lambda_{1\lim}^2+\lambda_{2\lim}^2+\lambda_{1\lim}^{-2}\lambda_{2\lim}^{-2}-3$, and NkT is the small-strain shear modulus. When $(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)/J_{\lim}\to 0$, the Taylor expansion gives $U(\lambda_1,\lambda_2,\lambda_3,T)=\frac{1}{2}NkT(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)$. That is, the Gent model recovers the neo-Hookean model when deformation is small compared to the limiting stretch. When $(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)/J_{\lim}\to 1$, the elastomer approaches the limiting stretch.

Eq. (33) gives out the specific free energy of the thermodynamic system of polar dielectric polymers. According to the derivation previously, we further investigate the constitutive relation and incompressible of the polar dielectric polymers.

5.2. Constitutive law

Substituting Eq. (33) into Eqs. (6)–(10), the nominal stress, the nominal electric field and the nominal local entropy density can be expressed respectively as follows:

$$\begin{aligned}\tilde{\sigma}_1=&NkT\lambda_1-\frac{\lambda_1^{-2}\lambda_2^{-1}\lambda_3\alpha(T-T_C)\tilde{D}^2}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]}\\&-\frac{b\lambda_1^{-1}\lambda_2^{-1}\lambda_3\alpha(T-T_C)\tilde{D}^2}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]^2}\end{aligned} \tag{34}$$

$$\begin{aligned}\tilde{\sigma}_2=&NkT\lambda_2-\frac{\lambda_1^{-1}\lambda_2^{-2}\lambda_3\alpha(T-T_C)\tilde{D}^2}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]}\\&-\frac{b\lambda_1^{-1}\lambda_2^{-1}\lambda_3\alpha(T-T_C)\tilde{D}^2}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]^2}\end{aligned} \tag{35}$$

$$\begin{aligned}\tilde{\sigma}_3=&NkT\lambda_3+\frac{\lambda_1^{-1}\lambda_2^{-1}\alpha(T-T_C)\tilde{D}^2}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]}\\&-\frac{(a+b)\lambda_1^{-1}\lambda_2^{-1}\lambda_3\alpha(T-T_C)\tilde{D}^2}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]^2}\end{aligned} \tag{36}$$

$$\tilde{E}=\frac{\lambda_1^{-1}\lambda_2^{-1}\lambda_3\alpha(T-T_C)\tilde{D}}{[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]} \tag{37}$$

$$\begin{aligned}\tilde{s}=&c\log(T/T_0)-\frac{1}{2}\frac{\lambda_1^{-1}\lambda_2^{-1}\lambda_3\alpha\tilde{D}^2}{[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]}\\&-\frac{1}{2}Nk(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)\end{aligned} \tag{38}$$

The equilibrium Eqs. (34)–(38) are based on nominal value of the thermodynamic system of polar dielectric polymers. According to the definition previously, we have the true stress, true electric field and true local entropy as follows

$$\sigma_1 = NkT\lambda_1\lambda_2^{-1}\lambda_3^{-1} - \frac{\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]} - \frac{b\lambda_1^{-1}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]^2} \tag{39}$$

$$\sigma_2 = NkT\lambda_2\lambda_1^{-1}\lambda_3^{-1} - \frac{\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]} - \frac{b\lambda_1^{-2}\lambda_2^{-1}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]^2} \tag{40}$$

$$\sigma_3 = NkT\lambda_3\lambda_1^{-1}\lambda_2^{-1} + \frac{\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]} - \frac{(a+b)\lambda_1^{-2}\lambda_2^{-2}\lambda_3\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]^2} \tag{41}$$

$$E = \frac{\lambda_1^{-1}\lambda_2^{-1}\alpha(T-T_C)D^{\sim}}{[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]} \tag{42}$$

$$s = \frac{c\log(T/T_0)}{\lambda_1\lambda_2\lambda_3} - \frac{1}{2}\frac{\lambda_1^{-2}\lambda_2^{-2}\alpha D^{\sim 2}}{[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]} - \frac{1}{2\lambda_1\lambda_2\lambda_3}Nk(\lambda_1^2+\lambda_2^2+\lambda_3^2-3) \tag{43}$$

Substituting Eq. (42) into Eqs. (39)–(41)and (43), since $D = D^{\sim}\lambda_1^{-1}\lambda_2^{-1}$, the item $\frac{\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]}$ in Eqs. (39)–(41) is altered into $\frac{\varepsilon(\lambda_1,\lambda_2,\lambda_3,T)E^2}{2}$, the item $\frac{b\lambda_1^{-1}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]^2}$ in Eqs. (39) is altered into $\frac{\partial\varepsilon(\lambda_1,\lambda_2,\lambda_3,T)}{2\partial\lambda_1}\lambda_1E^2$, and the third term in Eqs. (40) and (41) is altered into $\frac{\partial\varepsilon(\lambda_1,\lambda_2,\lambda_3,T)}{2\partial\lambda_2}\lambda_2E^2$, $\frac{\partial\varepsilon(\lambda_1,\lambda_2,\lambda_3,T)}{2\partial\lambda_3}\lambda_3E^2$, respectively. Eq. (43) $\frac{\lambda_1^{-2}\lambda_2^{-2}\alpha D^{\sim 2}}{2[1+a(\lambda_3-1)+b(\lambda_1+\lambda_2+\lambda_3-3)]}$ is altered into $\frac{\varepsilon(\lambda_1,\lambda_2,\lambda_3,T)E^2}{2(T-T_C)}$. If the stretch and temperature are fixed, Eq. (42) denotes the linear relation between the real electric displacement and the real electric field. Since Eqs. (39)–(41) have similar expressions, as an example, only Eq. (39) will be discussed in details in the following part. On the right side of Eq. (39), the first item is related to the elasticity, and the second item represents Maxwell stress, whose direction is the same as that of the imposed electric field. The third term is presented when the permittivity of dielectric elastomer varies with the stretch, which can be either tensile or compressive.

5.3. Incompressibility

Considering the incompressible of the polar dielectric polymers, that is $\lambda_3 = \lambda_1^{-1}\lambda_2^{-1}$, we get the following expressions based on Eqs. (20)–(27):

$$\sigma_1^{\sim} - \frac{\sigma_3^{\sim}}{\lambda_1^2\lambda_2} = NkT(\lambda_1 - \lambda_1^{-3}\lambda_2^{-2}) - \frac{\lambda_1^{-3}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]} - \frac{[b-(b+a)\lambda_1^{-2}\lambda_2^{-1}]\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]^2} \tag{44}$$

$$\sigma_2^{\sim} - \frac{\sigma_3^{\sim}}{\lambda_1\lambda_2^2} = NkT(\lambda_2 - \lambda_1^{-2}\lambda_2^{-3}) - \frac{\lambda_1^{-2}\lambda_2^{-3}\alpha(T-T_C)D^{\sim 2}}{[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]} - \frac{[b-(b+a)\lambda_1^{-1}\lambda_2^{-2}]\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]^2} \tag{45}$$

$$E^{\sim} = \frac{\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim}}{[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]} \tag{46}$$

$$s^{\sim} = c\log(T/T_0) - \frac{1}{2} \times \frac{\lambda_1^{-2}\lambda_2^{-2}\alpha D^{\sim 2}}{[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]} - \frac{1}{2}Nk(\lambda_1^2+\lambda_2^2+\lambda_1^{-2}\lambda_2^{-2}-3) \tag{47}$$

The true stress, the true electric filed and the true local entropy can be expressed as followings

$$\sigma_1 - \sigma_3 = NkT(\lambda_1 - \lambda_1^{-3}\lambda_2^{-2}) - \frac{\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]} - \frac{[b-(b+a)\lambda_1^{-2}\lambda_2^{-1}]\lambda_1^{-1}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]^2} \tag{48}$$

$$\sigma_2 - \sigma_3 = NkT(\lambda_2^2 - \lambda_1^{-2}\lambda_2^{-2}) - \frac{\lambda_1^{-2}\lambda_2^{-2}\alpha(T-T_C)D^{\sim 2}}{[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]} - \frac{[b-(b+a)\lambda_1^{-1}\lambda_2^{-2}]\lambda_1^{-2}\lambda_2^{-1}\alpha(T-T_C)D^{\sim 2}}{2[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]^2} \tag{49}$$

$$E = \frac{\lambda_1^{-1}\lambda_2^{-1}\alpha(T-T_C)D^{\sim}}{[1+a(\lambda_1^{-1}\lambda_2^{-1}-1)+b(\lambda_1+\lambda_2+\lambda_1^{-1}\lambda_2^{-1}-3)]} \tag{50}$$

$$s = c\log(T/T_0) - \frac{1}{2} \times \frac{\lambda_1^{-2}\lambda_2^{-2}\alpha D^{\sim 2}}{[1 + a(\lambda_1^{-1}\lambda_2^{-1} - 1) + b(\lambda_1 + \lambda_2 + \lambda_1^{-1}\lambda_2^{-1} - 3)]} - \frac{1}{2}Nk(\lambda_1^2 + \lambda_2^2 + \lambda_1^{-2}\lambda_2^{-2} - 3) \quad (51)$$

Similar to the derivations above, Eqs. (48)–(51) can be simplified.

$$\sigma_1 - \sigma_3 = NkT(\lambda_1 - \lambda_1^{-3}\lambda_2^{-2}) - \varepsilon(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)E^2 - \frac{\varepsilon(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)[b\lambda_1 - (b + a)\lambda_1^{-1}\lambda_2^{-1}]}{2}E^2 \quad (52)$$

$$\sigma_2 - \sigma_3 = NkT(\lambda_2^2 - \lambda_1^{-2}\lambda_2^{-2}) - \varepsilon(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)E^2 - \frac{\varepsilon(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)[b\lambda_2 - (b + a)\lambda_1^{-1}\lambda_2^{-1}]}{2}E^2 \quad (53)$$

$$E = \frac{\alpha(T - T_C)D}{[1 + a(\lambda_1^{-1}\lambda_2^{-1} - 1) + b(\lambda_1 + \lambda_2 + \lambda_1^{-1}\lambda_2^{-1} - 3)]} \quad (54)$$

$$s = c\log(T/T_0) - \frac{\varepsilon(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, T)E^2}{2\alpha(T - T_C)^2} - \frac{1}{2}Nk(\lambda_1^2 + \lambda_2^2 + \lambda_1^{-2}\lambda_2^{-2} - 3) \quad (55)$$

Fig. 3 shows the relation of work conjugate parameters between temperature and entropy of the thermodynamic system of polar elastic dielectric, where Fig. 3(a) represents the constant stretch condition and Fig. 3(b) represents the constant electric field condition.

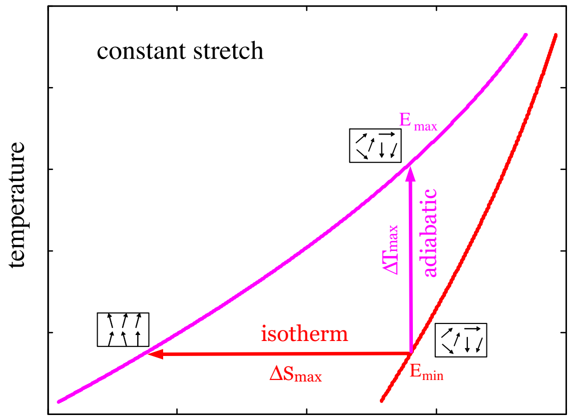
As shown in Fig. 3(a), at the initial temperature, without electric field, the dipole of polar dielectric is chaotic, indicating a relatively high entropy condition at this time. During the application of electric field, polar dielectric can reach the critical breakdown electric field $E_{\max}$ in two different routes: isothermal and adiabatic process.

In the isothermal process, with the increase of electric field, the entropy of the dielectric will decrease due to the orientation arrangement of dipole. When the critical breakdown eclectic field is reached, the dielectric has minimum entropy and maximum entropy change, which is $\Delta S_{\max}(E)$.

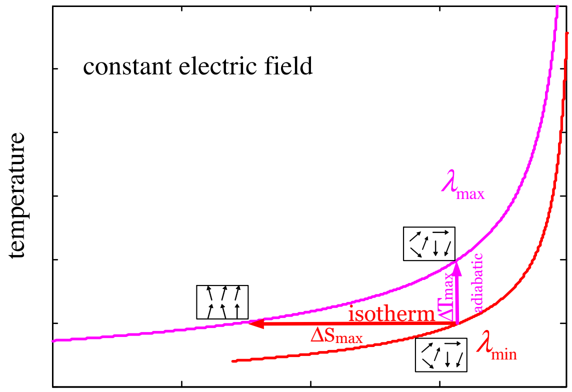
In the adiabatic process, with the increase of electric field, the temperature of dielectric will increase. When the critical breakdown electric field is reached, the dielectric has maximum temperature and maximum temperature change, which is $\Delta T_{\max}(E)$.

From Fig. 3(a) we can see that the influencing factors of polar dielectric include electric field and temperature. When the temperature change is small, we can ignore its influence, but when analyzing large electrocaloric effect of polar dielectric, we need to consider the influence of temperature.

Similarly, as shown in Fig. 3(b), at the original temperature, when the stretching $\lambda_{\lim}$ is small, the dipole of polar dielectric is chaotic. The entropy of dielectric is high at this moment. During the application of mechanical force, the polar dielectric can reach stretching limit $\lambda_{\max}$ in two different routes: isothermal process and adiabatic process.



(a) entropy



(b) entropy

Fig. 3. The temperature vs. the entropy of polar-elastic dielectrics under (a) constant stretch (b) constant electric field.

In the constant temperature process, with the increase of mechanical force, the entropy of dielectric will decrease because the inner arrangement of molecular chain is in order. When the stretching limit $\lambda_{\max}$ is reached, the entropy reaches its minimum value, while the entropy change $\Delta S_{\max}(\lambda)$ is maximum.

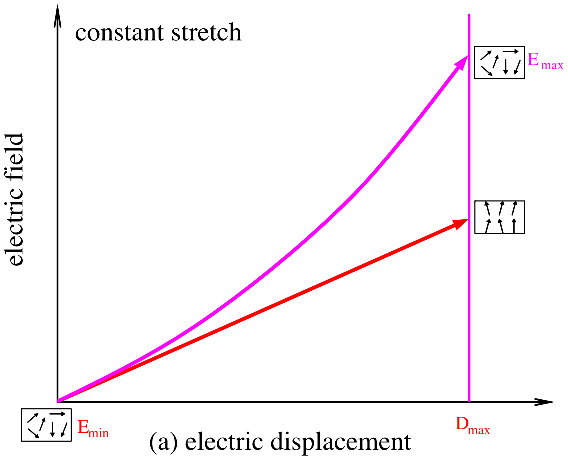
In the adiabatic process, with the increase of mechanical force, the temperature of dielectric will increase. When the stretching limit $\lambda_{\max}$ is reached, the temperature of dielectric reaches its maximum value, while the temperature change $\Delta T_{\max}(\lambda)$ is the maximum.

It could be seen from Fig. 3(b) that the influencing factors of the entropy of polar dielectric include temperature and stretching. When the deformation is relatively small, we can ignore its influence, but when analyzing polar dielectric within large deformation, we need to consider the influence of deformation.

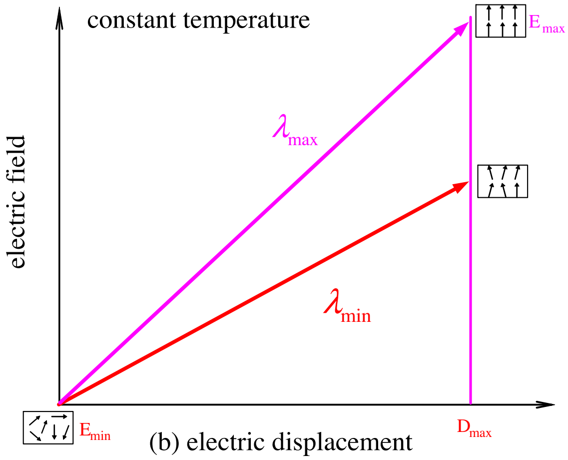
Fig. 4 shows another group of work conjugate parameters of the thermodynamic system of polar elastic dielectric, namely the relation between electric field and electric displacement. Fig. 4(a) indicates the condition of constant stretching while Fig. 4(b) is the condition of constant temperature. Here we use electric field and electric displacement to describe the two kinds of physical processes when applying voltage to polar elastic dielectric: isothermal process and the adiabatic process.

As indicated in Fig. 4(a), under electric field, the electric displacement increases from 0 to the breakdown charge $D_{\max}$. A constant gradient line indicates the constant temperature process, while an increasing gradient line indicates the adiabatic process. The gradient is determined by temperature, namely a high temperature lead to a large gradient. Here we suppose $D_{\max}$ is a straight line, while in fact, $D_{\max}$ is a curve influenced by the temperature. We ignored this influence in the schematic diagram.

As shown in Fig. 4(b), the electric displacement increases from 0 to $D_{\max}$ along two different lines. We consider $\lambda_{\min}$ and $\lambda_{\max}$ as constant. As an example, for the dielectric belong to neo-Hookean model, we can get the electrostriction parameter a and b (usually negative), and the absolute value is very small. For this reason, when the temperature is constant, we can see from Eq. (54) that large gradient corresponding to large stretching. In addition, the entropy of polar elastic dielectric is larger in the condition of small stretching and low electric field.



(a) electric displacement



(b) electric displacement

Fig. 4. The electric field vs. electric displacement of polar-elastic dielectrics under (a) constant stretch (b) constant temperature.

Fig. 5 shows the relation between work conjugate parameters, namely the nominal stress and stretching, in polar elastic dielectric thermodynamic system. Fig. 5(a) indicates the constant stretching condition while figure (b) indicates the constant electric field condition.

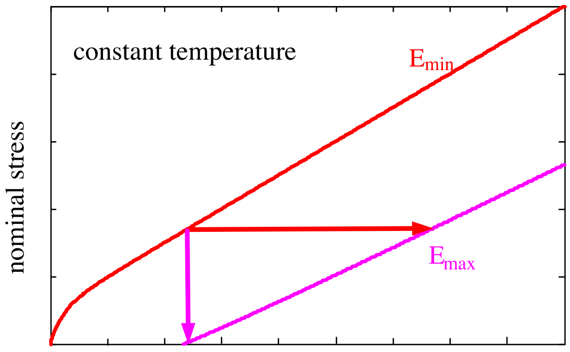
From Fig. 5(a), we can see that under the condition of equal stretching, when the electric field is low, the nominal stress of polar elastic dielectric is large.

6. Cooling devices based on large electrocaloric effect and deformation

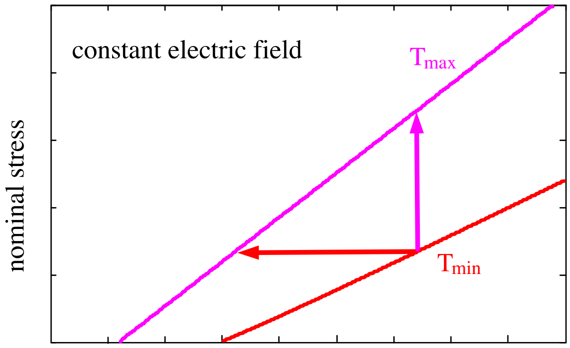
Fig. 6 describes the working principle of polar elastic dielectric as cooling devices, where Fig. 6(a) and (b) represents the constant stretching condition and Fig. 6(c) and (d) shows the non-constant stretching condition.

To describe the thermodynamic cycle, electric displacement and electric field are selected as parameters in Fig. 6(a), and entropy and temperature are selected in Fig. 6(b). The working material experiences four thermodynamic paths composing an analog to the Carnot cycle of a steam engine.

(1) In the adiabatic temperature rising process 1 → 2, the applied electric field on polar dielectric E_1 increases.



(a) stretch



(b) stretch

Fig. 5. The nominal stress vs. stretch of polar-elastic dielectrics under (a) constant temperature (b) constant electric field.

Due to the ECE, the material temperature rises, and the corresponding material changes from state 1 (E_1, T_1, S_2) to state 2 $(E_1\uparrow, T_2, S_2)$. ΔT represents the adiabatic temperature change from T_1 to T_2, $\Delta T = T_2 - T_1$ $(T_2 > T_1)$. This is an isentropic process.

(2) In the isothermal heat release process $2 \rightarrow 3$, the applied electric field on polar dielectric increases to E_2. The material changes from state 2 $(E_1\uparrow, T_2, S_2)$ to state 3 (E_2, T_2, S_1) with the entropy decreases, and the heat is ejected to the environment. ΔS donates the isothermal entropy change from S_1 to S_2, i.e. $\Delta S = S_2 - S_1$ $(S_2 > S_1)$.

(3) In the adiabatic temperature decreasing process $3 \rightarrow 4$, the applied electric field on polar dielectric decreases from E_2. The material changes from state 3 (E_2, T_2, S_1) to state 4 $(E_2\downarrow, T_1, S_1)$ with temperature decreasing. ΔT represents adiabatic temperature change from T_2 to T_1. This is an isentropic process.

(4) In the isothermal heat absorbing process $4 \rightarrow 1$, the applied electric field on polar dielectric decreases to E_1. The material changes from state 4 $(E_2\downarrow, T_1, S_1)$ to state 1 (E_1, T_1, S_2) with the entropy increases, and the heat is absorbed by the dielectric material. ΔS is the isothermal entropy change from S_1 to S_2. When the entire cycle completes, the working material backs to its original state and the next cycle is initiated.

In the isothermal decalescence process $4 \rightarrow 1$, the heat that polar dielectric absorbs from the environment is $\Delta q = T_1 \Delta S$, which shows its capability of absorbing heat energy. In the isothermal releasing process $2 \rightarrow 3$, the heat is ejected to the environment, which is $\Delta q^{/} = T_2 \Delta S$. Based on the first law of thermodynamics, the mechanical work that the environment generates on the working material is $\Delta q^{/} - \Delta q$. Thus, $\Delta W = \Delta T \Delta S$, which is known as the refrigerant capacity (RC) value.

As shown in Fig. 6(c) and (d), due to the applied electric field, the polar elastic dielectric would undergo large deformation (namely the stretch induced geometry change of the working material), and further lead to its entropy change. Therefore, entropy change shown in Fig. 6(c) and (d) is larger in comparison with that in Fig. 6(a) and (b), which further justifies our above mentioned analysis. That is, because of the coupling influence of electric field, temperature and large deformation, larger entropy change would be induced in polar elastic dielectric when subjected

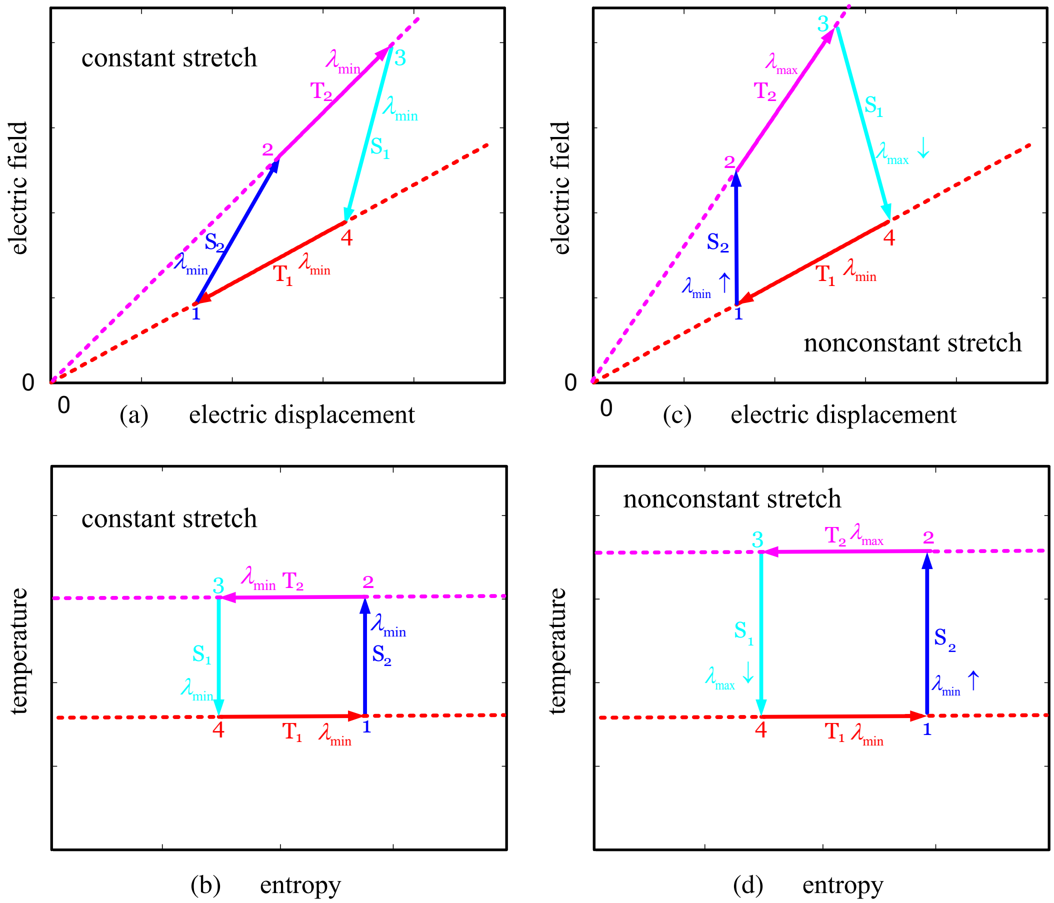


Fig. 6. Working cycle of polar elastic dielectric as cooling device under (a,b) constant stretch and (c,d) non-constant stretch.

to an external electric field. The result reveals the great potential of polar elastic dielectric in design and fabrication cooling devices with excellent performance.

The area of the allowable states of polar elastic dielectric as cooling device is demonstrated in Fig. 7, where Fig. 7(a) is described by the electric field-electric displacement plane, and Fig. 7(b) is described by the entropy–temperature plane. Here, we take the constant stretching condition as an example.

In Fig. 7, $T_{\min}$, and $T_{\max}$ donate the high and low temperature limit (namely the failure temperature of the material), respectively. T_1 is the initial working temperature of material. E_1 is the initial working voltage of the material ($E_{\min} = 0$, $E_1 > E_{\min}$), $E_{\max}$ is the breakdown voltage of the material, and E_2 is the current working voltage ($E_2 < E_{\max}$, and the magnitude of E_2 is the same order as that of breakdown voltage $E_2 < E_{\max}$). Due to the ECE, the temperature of working material reaches T_2, which is dependent on the intensity of polarization. The area surrounded by curves E_1, T_1, E_2 and T_2 is the allowable area of polar dielectric under the combination effect of a voltage and a temperature. In the allowable area, a point in such a plane represents a thermodynamic state of the polar dielectric under different temperature and voltage, and a curve represents thermodynamic process. Any cycle in the area is a possible thermodynamic cycle of system.

Three typical thermodynamic cycles of polar elastic dielectric as thermoelectricity energy transducer are plotted in Fig. 8.

In Fig. 8(a), the first cycle includes two adiabatic processes (1 → 2, 3 → 4) and two isothermal processes (2 → 3, 4 → 1), which is similar to the Carnot cycle of the steam engine. Considering the maximal change of temperature in polar dielectric caused by ECE, we can further determine the heat Δq absorbed from outside and the work ΔW produced by outside. We call it the similar Carnot cycle with maximal temperature change.

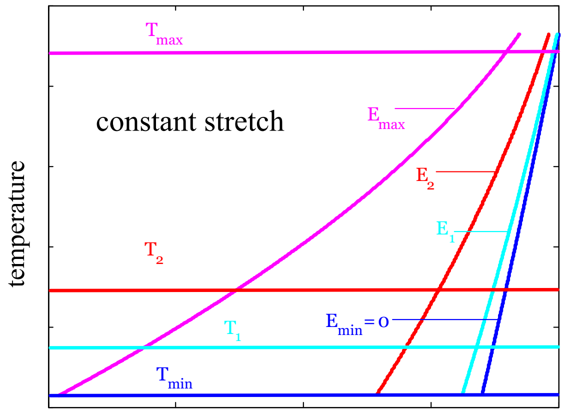
In Fig. 8(b), the second cycle also concludes two adiabatic processes (1 → 2, 3 → 4) and two isothermal processes (2 → 3, 4 → 1). Considering the maximal work produced by the outside, say ΔW, we can further determine the temperature change, entropy change ΔS and heat Δq absorbed from outside of the polar dielectric. We call it the similar Carnot cycle with maximal work.

As Fig. 8(c) shows, the third cycle is surrounded by curves T_1, E_1, T_2 and E_2, which represents the allowable area of polar dielectric. This kind of cycle includes two isothermal processes (2 → 3, 4 → 1) and two voltage-constant processes (1 → 2, 3 → 4).

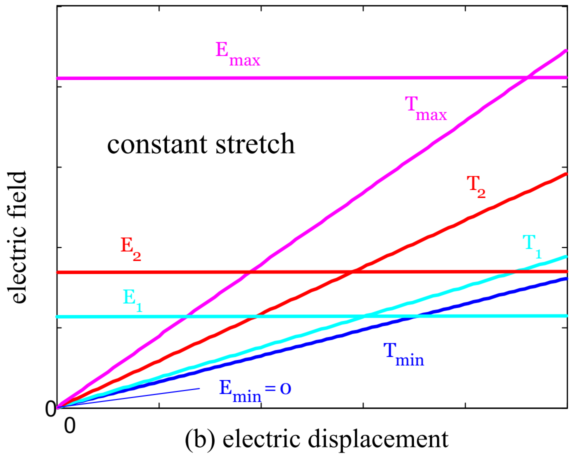
To realize this cycle we need to design a special physical process as follows:

From state 1 to state 2, the electric field is insured to be constant on the polar dielectric. Increasing the temperature from T_1 to T_2, the entropy would increase. State 2 to state 3 is an exothermic process.

Keeping the temperature of the polar dielectric as constant, and increasing the voltage from E_1 to E_2, the molecular dipole turns from disordered state to ordered state with the entropy decrease.



(a) entropy



(b) electric displacement

Fig. 7. Area of allowable states of polar elastic dielectric as cooling device.

From state 3 to state 4, keeping the electric field on polar dielectric as constant, and decreasing the temperature from T_2 to T_1, the entropy keeps decreasing.

In the last process: state 4 to state 1, remaining the temperature of dielectric material as constant, and decreasing the voltage from E_2 to E_1, the entropy would increase. The polar dielectric absorbs heat from outside which leads to the purpose of cooling. We call this cycle the similar Otto cycle with maximal work as combustion engine.

We next focus on similar Otto cycle with maximal work as combustion engine. After applying the electric field, the polar elastic dielectric would undergo iso-biaxial deformation, namely $\lambda_1 = \lambda_2 = \lambda_e$, where λ_e is the electric induced deformation. According to Eqs. (54) and (55), the relation between stretch and electric field is shown as following:

$$s = c\log(T/T_0) - \frac{[1 + a(\lambda_e^{-2} - 1) + b(2\lambda_e + \lambda_e^{-2} - 3)]}{2\alpha(T - T_C)^2}E^2 - \frac{1}{2}Nk(2\lambda_e + \lambda_e^{-4} - 3) \tag{56}$$

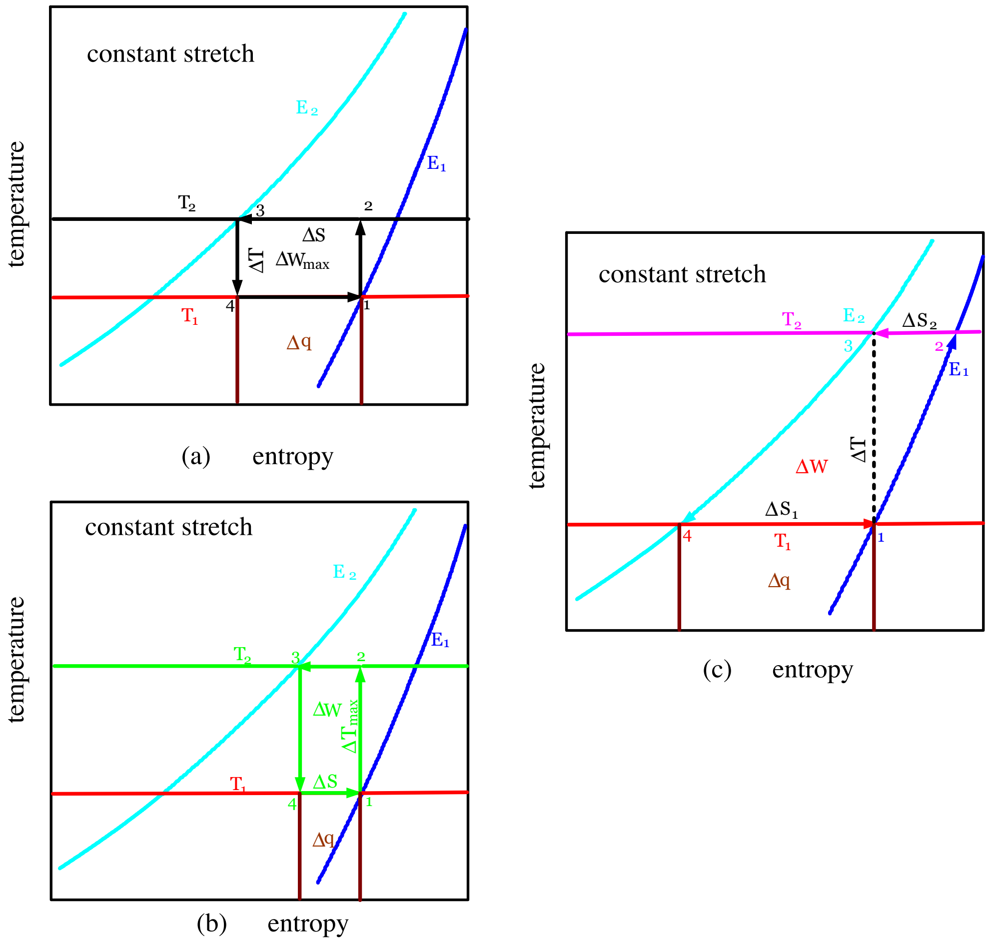


Fig. 8. Several typical thermodynamic cycles of the polar elastic dielectric as cooling device.

When $T_1 > T_C$, considering the polar dielectric cooling devices going through similar Otto thermodynamic cycle of maximal work, for simplicity, let $E_1 = 0$. In Fig. 8(c), point (1), $S_1 = c\log(T_1/T_0)$, point (3),

$$S_3 = c\log(T_2/T_0) - \frac{[1 + a(\lambda_e^{-2} - 1) + b(2\lambda_e + \lambda_e^{-2} - 3)]}{2\alpha(T_2 - T_C)^2}E_2^2 - \frac{1}{2}Nk(2\lambda_e + \lambda_e^{-4} - 3)$$

according to $S_1 = S_3$, we obtain,

$$c\log\left(\frac{T_2}{T_1}\right) = \frac{[1 + a(\lambda_e^{-2} - 1) + b(2\lambda_e + \lambda_e^{-2} - 3)]}{2\alpha(T_2 - T_C)^2}E_2^2 + \frac{1}{2}Nk(2\lambda_e + \lambda_e^{-4} - 3) \tag{57}$$

Therefore, $\Delta T_{\max} = f\left[\frac{[f(\lambda_e)]E_2^2}{\alpha c}, T_1\right]$. Point (2), $S_2 = c\log(T_2/T_0)$, point (4),

$$S_4 = c\log(T_1/T_0) - \frac{[1 + a(\lambda_e^{-2} - 1) + b(2\lambda_e + \lambda_e^{-2} - 3)]}{2\alpha(T_1 - T_C)^2}E_2^2 - \frac{1}{2}Nk(2\lambda_e + \lambda_e^{-4} - 3)$$

In Fig. 8(c),

$$\Delta S_1 = S_1 - S_4 = \frac{[1 + a(\lambda_e^{-2} - 1) + b(2\lambda_e + \lambda_e^{-2} - 3)]}{2\alpha(T_1 - T_C)^2}E_2^2 + \frac{1}{2}Nk(2\lambda_e + \lambda_e^{-4} - 3)$$

$$\Delta S_2 = S_2 - S_3 = \frac{[1 + a(\lambda_e^{-2} - 1) + b(2\lambda_e + \lambda_e^{-2} - 3)]}{2\alpha(T_2 - T_C)^2}E_2^2 + \frac{1}{2}Nk(2\lambda_e + \lambda_e^{-4} - 3)$$

The work is

$$\Delta W = T_2\Delta S_2 - T_1\Delta S_1 = \left\{\frac{[1 + a(\lambda_e^{-2} - 1) + b(2\lambda_e + \lambda_e^{-2} - 3)]E_2^2}{2\alpha} + \frac{1}{2}Nk(2\lambda_e + \lambda_e^{-4} - 3)\right\}\left[\frac{T_2}{(T_2 - T_C)^2} - \frac{T_1}{(T_1 - T_C)^2}\right] \tag{58}$$

and the heat absorbed from the outside is

$$\Delta q = \left\{ \frac{[1 + a(\lambda_e^{-2} - 1) + b(2\lambda_e + \lambda_e^{-2} - 3)]}{2\alpha(T_1 - T_C)^2} E_2^2 + \frac{1}{2} Nk(2\lambda_e + \lambda_e^{-4} - 3) \right\} T_1 \tag{59}$$

7. Generator based on large pyroelectric effect and deformation

Fig. 9 describes the working principle of polar elastic dielectric as generator, where Fig. 9(a) and (b) represents the constant stretching condition, and Fig. 9(c) and (d) represents the non-constant stretching condition.

To describe the thermodynamic cycle, voltage and electric charge are selected as parameters in Fig. 9(a), and entropy and temperature are selected in Fig. 9(b). The working material experiences four thermodynamic paths composing an analog to the Carnot cycle of a steam engine.

(1) In the constant electric quantity and voltage increasing process 1 → 2, the applied thermal field on polar dielectric T_1 increases. Due to the PCE (or ECE), the material voltage rises, and the corresponding material changes from state 1 (T_1, Φ_1, Q_1) to state 2 $(T_1 \uparrow, \Phi_2, Q_1)$. $\Delta\Phi$ represents voltage change from Φ_1 to Φ_2 under constant electric quantity, $\Delta\Phi = \Phi_2 - \Phi_1$ $(\Phi_2 > \Phi_1)$. This is a constant electric quantity process.

(2) In the constant voltage and discharging process 2 → 3, the applied thermal field on polar dielectric increases to T_2. The material changes from state 2 $(T_1 \uparrow, \Phi_2, Q_1)$ to state 3 (T_2, Φ_2, Q_2) with the electric quantity decreases, and the electric charge is released to the environment. ΔQ denotes the electric quantity change from Q_1 to Q_2 under constant voltage, i.e. $\Delta Q = Q_1 - Q_2$ $(Q_1 > Q_2)$.

(3) In the constant electric quantity and voltage decreasing process 3 → 4, the applied thermal field on polar dielectric decreases from T_2. The material changes from state 3 (T_2, Φ_2, Q_2) to state 4 $(T_2 \downarrow, \Phi_1, Q_2)$ with voltage decreasing. $\Delta\Phi$ represents voltage change from Φ_2 to Φ_1 under constant electric quantity. This is a constant electric quantity process.

(4) In the constant voltage and charging absorbing process 4 → 1, the applied thermal field on polar dielectric decreases to T_1. The material changes from state 4 $(T_2 \downarrow, \Phi_1, Q_2)$ to state 1 (T_1, Φ_1, Q_1) with the electric quantity increases, and the electric charge is absorbed by the dielectric material.

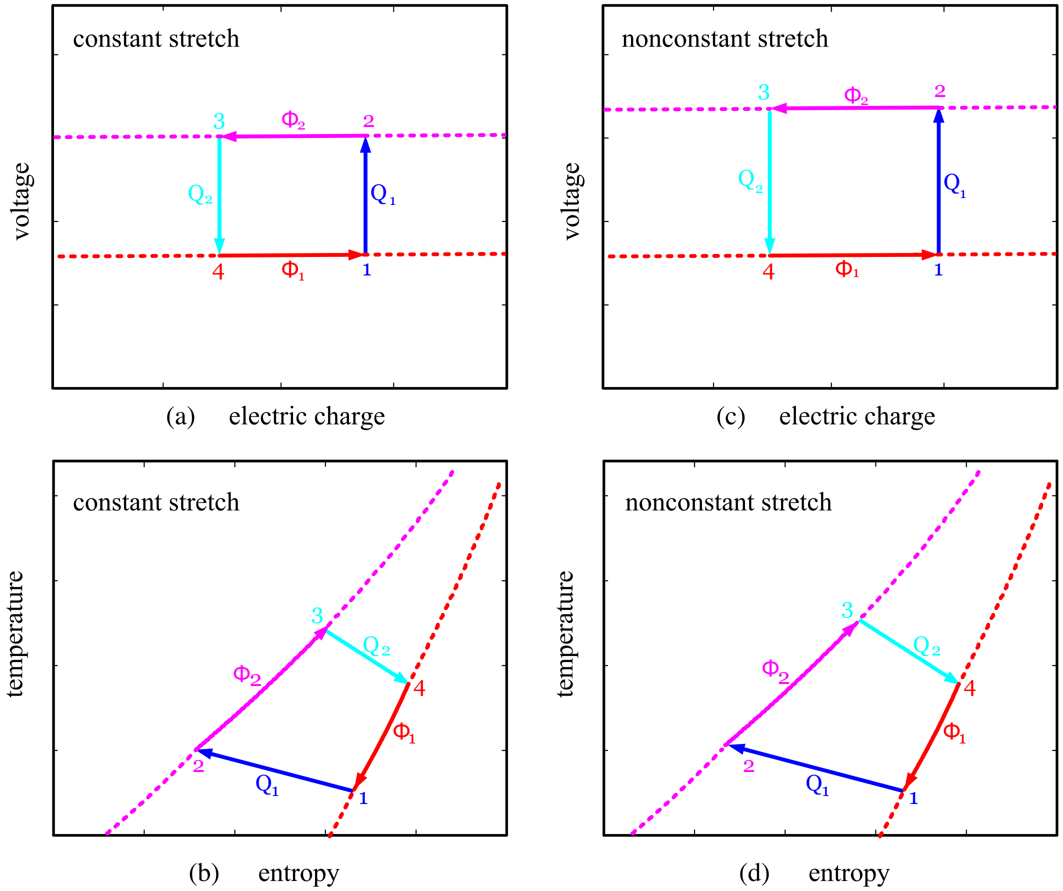


Fig. 9. Working cycle of polar elastic dielectric as generator under (a,b) constant stretch and (c,d) non-constant temperature.

When the entire cycle completes, the working material backs to its original state and the next cycle is initiated.

In the constant voltage and charging process 4 → 1, the environment produces work to the working material, namely the energy collection of the generator. The collected energy is $\Phi_1 \Delta Q$.

In the constant voltage and discharging process 2 → 3, the electric quantity ΔQ is released into the environment. The electric quantity variation is ΔQ, and the corresponding energy variation is $\Phi_2 \Delta Q$.

Similarly, based on the first law of thermodynamics, the work that the environment does on the working material is $\Delta W = \Delta\Phi\Delta Q$.

As shown in Fig. 9(c) and (d), when a thermal filed is applied to the polar elastic dielectric, electric charge would be induced in the working material due to the ECE. Subsequently, the working material would be stretched under the Maxwell force. At this moment, the polar elastic dielectric could be considered as a variable capacitor. Because of the increase of film area and decrease of film thickness, the capacitance and the stored electric quantity would be increased under constant voltage (similar with the above mentioned discussions, the entropy of the material is also changed). Therefore, the electric quantity variation in Fig. 9(c) and (d) is larger than that in Fig. 9(a) and (b). It is concluded that due to the coupling influence of temperature and large deformation, larger electric quantity would be induced in the polar elastic dielectric after being subjected to thermal filed. The result reveals the application potential of polar elastic dielectric in design and fabrication of energy generators with higher performance.

Three typical thermodynamic cycles of polar elastic dielectric as energy generator are plotted in Fig. 10. As shown in Fig. 10(a), the first cycle includes two constant voltage processes (1 → 2, 3 → 4) and two constant electric quantity processes (2 → 3, 4 → 1), which is similar to the Carnot cycle of the steam engine. The voltage variation of the energy generator $\Delta\Phi$ in this cycle is maximal due to the consideration of ECE. Furthermore, we can also determine the electric quantity variation ΔQ of the energy generator. The collected energy is denoted as $\Phi_1 \Delta Q$, and the work produced by the environment to the working material is $\Delta W = \Delta\Phi\Delta Q$. We call it the similar Carnot cycle with maximal voltage change.

Similarly, in the second cycle, another similar Carnot cycle also experiences two constant voltage processes (1 → 2, 3 → 4) and two constant electric quantity processes (2 → 3, 4 → 1) as shown in Fig. 10(b). Considering the ECE, the energy variation of the energy generator $\Delta W_{\max}$ is maximal in this cycle. Furthermore, we can also determine the voltage variation $\Delta\Phi$ of the energy generator, the electric quantity variation ΔQ and the collected energy $\Phi_1 \Delta Q$. We call it the similar Carnot cycle with maximal work.

Similar with the above mentioned analysis, as shown in Fig. 10(c), a practical physical process should be designed to realize the third cycle, which is similar with Otto cycle experiencing two isothermal processes and constant pressure processes. We call this cycle the similar Otto cycle with maximal work as combustion engine. In the electric charge–voltage plane, allowable area of polar elastic dielectric as energy generator is surrounded by curves T_1, Φ_1, T_2 and Φ_2. In the allowable area, a point in such a plane represents a thermodynamic state of the polar dielectric under specified temperature and voltage, and a curve represents thermodynamic process. Any cycle in the area is possible thermodynamic cycles of system.

Here, the voltage variation after the polar elastic dielectric is subjected to thermal filed is reflected by $\Delta\Phi$, which is related with the ECE of the dielectric material. It could be used to determine the voltage variation range of the established energy generator based on this material. ΔQ_2 represents the variation of electric quantity after the working material is subjected to a voltage of Φ_2, and its temperature is decreased from T_2 to T_1. It could be used to measure the electric quantity variation during the discharging process of the energy generator. ΔQ_1 represents the variation of electric quantity after the working material is subjected to a voltage of Φ_1, and its temperature is decreased from T_2 to T_1. It could be used to measure the collected electric quantity of the energy generator. $\Phi_2 \Delta Q_2$ denotes the discharged electric quantity of the energy generator, and $\Phi_1 \Delta Q_1$ denotes the collected energy. Based on the first law of thermodynamics, $\Delta W = \Phi_2 \Delta Q_2 - \Phi_1 \Delta Q_1$, which could be used to reflect the work produced by the environment on the working material.

When $T_1 > T_C$, we consider the polar dielectric generators going through similar Otto thermodynamic cycle of maximal work. In Fig. 10(c), point (1),

$$Q_1 = \frac{\Phi_1}{L_1 L_2 L_3} \frac{[1 + a(\lambda_{e1}^{-2} - 1) + b(2\lambda_{e1} + \lambda_{e1}^{-2} - 3)]}{\alpha(T_1 - T_C)\lambda_{e1}^2}$$

point (3),

$$Q_3 = \frac{\Phi_2}{L_1 L_2 L_3} \frac{[1 + a(\lambda_{e2}^{-2} - 1) + b(2\lambda_{e2} + \lambda_{e2}^{-2} - 3)]}{\alpha(T_2 - T_C)\lambda_{e2}^2}$$

Here, λ_{e1} and λ_{e2}, respectively denote the iso-biaxial deformation of the polar elastic dielectric under the voltage of Φ_1 and Φ_2. L_1, L_2 and L_3 represents the dimension of the energy generator in the three principal direction. According to $Q_1 = Q_3$, we obtain,

$$\frac{\Phi_2}{\Phi_1} = \left[\frac{1 + a(\lambda_{e1}^{-2} - 1) + b(2\lambda_{e1} + \lambda_{e1}^{-2} - 3)}{1 + a(\lambda_{e2}^{-2} - 1) + b(2\lambda_{e2} + \lambda_{e2}^{-2} - 3)}\right] \frac{(T_2 - T_C)\lambda_{e2}^2}{(T_1 - T_C)\lambda_{e1}^2} \tag{60}$$

Therefore, $\Delta\Phi_{\max} = f(T_2, T_1, \lambda_{e2}, \lambda_{e1})$. Point (2),

$$Q_2 = \frac{\Phi_2}{L_1 L_2 L_3} \frac{[1 + a(\lambda_{e2}^{-2} - 1) + b(2\lambda_{e2} + \lambda_{e2}^{-2} - 3)]}{\alpha(T_1 - T_C)\lambda_{e2}^2}$$

point (4),

$$Q_4 = \frac{\Phi_1}{L_1 L_2 L_3} \frac{[1 + a(\lambda_{e1}^{-2} - 1) + b(2\lambda_{e1} + \lambda_{e1}^{-2} - 3)]}{\alpha(T_2 - T_C)\lambda_{e1}^2}$$

In Fig. 10(c),

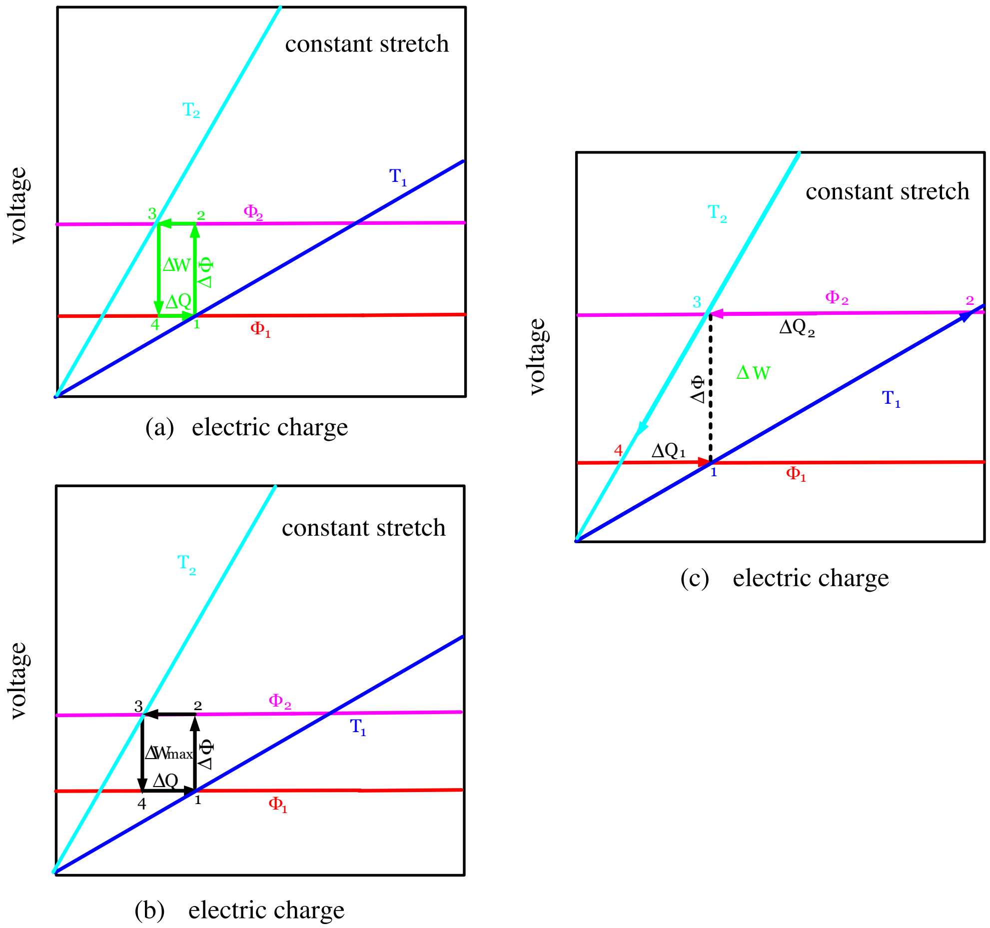


Fig. 10. Several typical thermodynamic cycles of the polar elastic dielectric as generators.

$$\Delta Q_1 = Q_1 - Q_4 = \frac{\Phi_1[1 + a(\lambda_{e1}^{-2} - 1) + b(2\lambda_{e1} + \lambda_{e1}^{-2} - 3)]}{L_1L_2L_3\alpha} \times \left[\frac{1}{(T_1 - T_C)\lambda_{e1}^2} - \frac{1}{(T_2 - T_C)\lambda_{e2}^2}\right]$$

$$\Delta Q_2 = Q_2 - Q_3 = \frac{\Phi_2[1 + a(\lambda_{e2}^{-2} - 1) + b(2\lambda_{e2} + \lambda_{e2}^{-2} - 3)]}{L_1L_2L_3\alpha} \times \left[\frac{1}{(T_1 - T_C)\lambda_{e1}^2} - \frac{1}{(T_2 - T_C)\lambda_{e2}^2}\right]$$

The work is

$$\Delta W = \Phi_2\Delta Q_2 - \Phi_1\Delta Q_1 = \left[\frac{1}{(T_1 - T_C)\lambda_{e1}^2} - \frac{1}{(T_2 - T_C)\lambda_{e2}^2}\right] \times \frac{\{\Phi_2^2[1 + a(\lambda_{e2}^{-2} - 1) + b(2\lambda_{e2} + \lambda_{e2}^{-2} - 3)] - \Phi_1^2[1 + a(\lambda_{e1}^{-2} - 1) + b(2\lambda_{e1} + \lambda_{e1}^{-2} - 3)]\}}{L_1L_2L_3\alpha} \tag{61}$$

According to the above mentioned study, the energy collected by the polar dielectric generator could be expressed as:

$$\Phi_1\Delta Q_1 = \frac{\Phi_1^2[1 + a(\lambda_{e1}^{-2} - 1) + b(2\lambda_{e1} + \lambda_{e1}^{-2} - 3)]}{L_1L_2L_3\alpha} \times \left[\frac{1}{(T_1 - T_C)\lambda_{e1}^2} - \frac{1}{(T_2 - T_C)\lambda_{e2}^2}\right] \tag{62}$$

8. The mechanical behavior of polar electric dielectric with large electrocaloric effect and deformation undergoing ferroelectric–paraelectric phase transition

8.1. Free energy of polar elastic dielectric

When the polar dielectric experiences ferroelectric–paraelectric phase transition ($T < T_C$), the polar electric dielectric undergoes the ferroelectric–paraelectric phase transition. Due to symmetry, we expand the free-energy function of polar dielectric $W(T, \lambda_1, \lambda_2, \lambda_3, D^{\sim})$ into the Taylor series in terms of $D^{\sim}$ up to the quartic term.

$$W(T, \lambda_1, \lambda_2, \lambda_3, D^{\sim}) = W_0(T) + W_1(T, \lambda_1, \lambda_2, \lambda_3) + \frac{1}{2}\eta(T, \lambda_1, \lambda_2, \lambda_3)D^{\sim 2} + \frac{1}{4}\pi(\lambda_1, \lambda_2, \lambda_3)D^{\sim 4} + \cdots \tag{63}$$

In Eq. (63), $W_0(T)$ is the thermal contribution, representing the influence of temperature on polar electric dielectric thermo-electro-mechanical coupling system. $W_1(\lambda_1, \lambda_2, \lambda_3)$ is the thermal elastic energy, representing the thermal hyperelastic energy of the polar electric dielectric. $\frac{1}{2}\eta(T, \lambda_1, \lambda_2, \lambda_3)D^{\sim 2}$ is the electric field energy, function $\eta(T, \lambda_1, \lambda_2, \lambda_3)$ reveals the influence of temperature and stretch on the electric field energy, and $\frac{1}{4}\pi(\lambda_1, \lambda_2, \lambda_3)D^{\sim 4} + \cdots$ describes the energy condition of polar electric dielectric undergoing phase transition.

8.2. Constitutive law of polar elastic dielectric

Substituting Eq. (63) into Eqs. (6)–(10), the nominal stress, the nominal electric field and the nominal local entropy density of the polar electric dielectric undergoing the ferroelectric–paraelectric phase transition can be expressed respectively as follows:

$$\sigma_1^{\sim} = \frac{\partial W_1(T, \lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_1} + \frac{1}{2}\frac{\partial \eta(T, \lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_1}D^{\sim 2} + \frac{1}{4}\frac{\partial \pi(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_1}D^{\sim 4} + \cdots \tag{64}$$

$$\sigma_2^{\sim} = \frac{\partial W_1(T, \lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_2} + \frac{1}{2}\frac{\partial \eta(T, \lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_2}D^{\sim 2} + \frac{1}{4}\frac{\partial \pi(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_2}D^{\sim 4} + \cdots \tag{65}$$

$$\sigma_3^{\sim} = \frac{\partial W_1(T, \lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_3} + \frac{1}{2}\frac{\partial \eta(T, \lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_3}D^{\sim 2} + \frac{1}{4}\frac{\partial \pi(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_3}D^{\sim 4} + \cdots \tag{66}$$

$$E^{\sim} = \eta(T, \lambda_1, \lambda_2, \lambda_3)D^{\sim} + \pi(\lambda_1, \lambda_2, \lambda_3)D^{\sim 3} + \cdots \tag{67}$$

$$s^{\sim} = -\frac{\partial W_0(T)}{\partial T} - \frac{\partial W_1(T, \lambda_1, \lambda_2, \lambda_3)}{\partial T} - \frac{1}{2}\frac{\partial \eta(T, \lambda_1, \lambda_2, \lambda_3)}{\partial T}D^{\sim 2} + \cdots \tag{68}$$

Furthermore, by submitting Eqs. (64)–(68) into Eqs. (11)–(13), the true stress, true electric field and true local entropy density could be expressed as followings:

$$\sigma_1 = \frac{\partial W_1(T, \lambda_1, \lambda_2, \lambda_3)}{\lambda_2\lambda_3\partial \lambda_1} + \frac{1}{2}\frac{\partial \eta(T, \lambda_1, \lambda_2, \lambda_3)}{\lambda_2\lambda_3\partial \lambda_1}D^{\sim 2} + \frac{1}{4}\frac{\partial \pi(\lambda_1, \lambda_2, \lambda_3)}{\lambda_2\lambda_3\partial \lambda_1}D^{\sim 4} + \cdots \tag{69}$$

$$\sigma_2 = \frac{\partial W_1(T, \lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_3\partial \lambda_2} + \frac{1}{2}\frac{\partial \eta(T, \lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_3\partial \lambda_2}D^{\sim 2} + \frac{1}{4}\frac{\partial \pi(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_3\partial \lambda_2}D^{\sim 4} + \cdots \tag{70}$$

$$\sigma_3 = \frac{\partial W_1(T, \lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_2\partial \lambda_3} + \frac{1}{2}\frac{\partial \eta(T, \lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_2\partial \lambda_3}D^{\sim 2} + \frac{1}{4}\frac{\partial \pi(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_2\partial \lambda_3}D^{\sim 4} + \cdots \tag{71}$$

$$E = \frac{1}{\lambda_3}[\eta(T, \lambda_1, \lambda_2, \lambda_3)D^{\sim} + \pi(\lambda_1, \lambda_2, \lambda_3)D^{\sim 3} + \cdots] \tag{72}$$

$$s = -\frac{\partial W_0(T)}{\lambda_1\lambda_2\lambda_3\partial T} - \frac{\partial W_1(T, \lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_2\lambda_3\partial T}\frac{1}{2} \times \frac{\partial \eta(T, \lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_2\lambda_3\partial T}D^{\sim 2} + \cdots \tag{73}$$

In Eqs. (64)–(68), the equilibrium functions of polar electric dielectric with large ECE and deformation undergoing ferroelectric–paraelectric phase transition are established by using nominal parameters, and in Eqs. (69)–(73), the equilibrium functions of the polar electric dielectric thermo-electro-mechanical system is given by using true parameters. In the Eqs. (64)–(73), if the expressions of functions $W_0(T)$, $W_1(T, \lambda_1, \lambda_2, \lambda_3)$, $\eta(T, \lambda_1, \lambda_2, \lambda_3)$ and $\pi(\lambda_1, \lambda_2, \lambda_3)$ are given, the nominal stress, true stress, nominal electric field, true electric field, nominal local entropy density and true nominal local entropy density could be subsequently derived.

By referring Eq. (32), we can choose $W_0(T)$ as the thermal contribution. $W_1(T, \lambda_1, \lambda_2, \lambda_3)$ could be selected as neo-Hookean hyperelastic model, referring Eq. (28). According to Eq. (33), we can obtain the expression of function $\eta(T, \lambda_1, \lambda_2, \lambda_3)$ as following:

$$\eta(T, \lambda_1, \lambda_2, \lambda_3) = \frac{1}{2}\frac{\alpha(T - T_C)\lambda_1^{-1}\lambda_2^{-1}\lambda_3}{[1 + a(\lambda_3 - 1) + b(\lambda_1 + \lambda_2 + \lambda_3 - 3)]} \tag{74}$$

In the following discussions, we try to give the expression of $\pi(\lambda_1, \lambda_2, \lambda_3)$. If the influence of polar dielectric deformation is ignored, when $T < T_C$, the polar dielectric goes through the ferroelectric–paraelectric phase transition. Due to symmetry, we expand the free-energy function of polar dielectric $W(T, D)$ into the Taylor series in terms of Dup to the quartic term:

$$W(T, D) = W_0'(T) + \frac{1}{2}\gamma D^2 + \frac{1}{4}\xi D^4 \tag{75}$$

Here, γ and ξ are phenomenology parameters. According to the relation between the true electric displacement and nominal electric displacement, and considering the influence of deformation, Eq. (75) could be rewritten as:

$$W(T,\lambda_1,\lambda_2,\lambda_3,\tilde{D}) = W_0'(T,\lambda_1,\lambda_2,\lambda_3) + \frac{1}{2}\gamma\tilde{D}^2\lambda_1^{-2}\lambda_2^{-2} + \frac{1}{4}\xi\tilde{D}^4\lambda_1^{-4}\lambda_2^{-4} \tag{76}$$

Here, $W_0'(T,\lambda_1,\lambda_2,\lambda_3) = W_0(T) + W_1(T,\lambda_1,\lambda_2,\lambda_3)$. Comparing Eqs. (76) and (63), $\pi(\lambda_1,\lambda_2,\lambda_3)$ could be selected as:

$$\pi(\lambda_1,\lambda_2,\lambda_3) = \xi\lambda_1^{-4}\lambda_2^{-4} \tag{77}$$

8.3. Polar elastic dielectric as cooling devices undergoing ferroelectric–paraelectric phase transition

Fig. 11 depicts the working cycle similar to Carnot of polar electric dielectric as cooling devices under different conditions: constant stretch condition, nonconstant stretch condition, undergoing ferroelectric phase and undergoing ferroelectric–paraelectric phase transition. From the figure, it could be found that the allowable area is larger in polar electric dielectric undergoing large deformation and phase transition, indicating that the working material after experiencing these two processes exhibits more obvious ECE, which is more suitable for the fabrication of cooling devices with excellent performance.

Subsequently, we focus on similar Otto cycle with maximal work as combustion engine in polar elastic dielectric undergoing ferroelectric–paraelectric phase transition ($T_L < T_C$). After subjected to an electric field, iso-biaxial deformation would be induced in the polar elastic dielectric, namely $\lambda_1 = \lambda_2 = \lambda_e$, where λ_e is the electro-induced deformation. Considering Eqs. (28), (32), (63) and (77), we could obtain the free energy function of the polar dielectric undergoing large deformation and ferroelectric–paraelectric phase transition

$$\begin{aligned} W(\lambda_e,T,\tilde{D}) = {} & \frac{1}{2}NkT(2\lambda_e^2+\lambda_e^{-4}-3) \\ & + c[(T-T_0) - T\log(T/T_0)] \\ & + \frac{\lambda_e^{-4}}{2[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]} \\ & \alpha(T-T_C)\tilde{D}^2 + \frac{1}{4}\xi\lambda_e^{-8}\tilde{D}^4 \end{aligned} \tag{78}$$

The relation between the nominal electric field and the nominal electric displacement is

$$\begin{aligned} \tilde{E} = {} & \frac{\lambda_e^{-4}}{[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]}\alpha(T-T_C)\tilde{D} \\ & + \xi\lambda_e^{-8}\tilde{D}^3 \end{aligned} \tag{79}$$

Considering the relation between the true electric field and nominal electric field, the relation between the true electric field and nominal electric displacement could be expressed as

$$\begin{aligned} E = {} & \frac{\lambda_e^{-6}}{[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]}\alpha(T-T_C)\tilde{D} \\ & + \xi\lambda_e^{-10}\tilde{D}^3 \end{aligned} \tag{80}$$

From Eq. (80), $\tilde{D} = f(E,T,\lambda_e)$. The entropy of polar dielectric undergoing ferroelectric–paraelectric phase transition could be expressed as:

$$\begin{aligned} s = {} & c\log(T/T_0) - \frac{\lambda_e^{-4}}{2[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]} \\ & \alpha[f(E,T,\lambda_e)]^2 - \frac{1}{2}Nk(2\lambda_e^2+\lambda_e^{-4}-3) \end{aligned} \tag{81}$$

When $T_1' < T_C$, considering the polar dielectric cooling devices going through similar Otto thermodynamic cycle of maximal work, For simplicity, let $E_1 = 0$. In Fig. 12(c), point (1), $S_1 = c\log(T_1'/T_0)$, point (3),

$$\begin{aligned} S_3 = {} & c\log(T_2'/T_0) \\ & - \frac{\lambda_e^{-4}}{2[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]}\alpha[f(E_2,T_2',\lambda_e)]^2 \\ & - \frac{1}{2}Nk(2\lambda_e^2+\lambda_e^{-4}-3) \end{aligned}$$

according to $S_1 = S_3$, we obtain,

$$\begin{aligned} c\log\left(\frac{T_2'}{T_1'}\right) = {} & \frac{\lambda_e^{-4}}{2[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]} \\ & \alpha[f(E_2,T_2',\lambda_e)]^2 + \frac{1}{2}Nk(2\lambda_e^2+\lambda_e^{-4}-3) \end{aligned} \tag{82}$$

Therefore, $\Delta T_{\max} = f\left\{\frac{[f(\lambda_e)][f(E_2,T_2',\lambda_e)]^2}{\alpha c}, T_1'\right\}$. Point (2), $S_2 = c\log(T_2'/T_0)$, point (4),

$$\begin{aligned} S_4 = {} & c\log(T_1'/T_0) \\ & - \frac{\lambda_e^{-4}}{2[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]}\alpha[f(E_2,T_1',\lambda_e)]^2 \\ & - \frac{1}{2}Nk(2\lambda_e^2+\lambda_e^{-4}-3) \end{aligned}$$

In Fig. 12(c),

$$\begin{aligned} \Delta S_1 & = S_1 - S_4 \\ & = \frac{\lambda_e^{-4}}{2[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]}\alpha[f(E_2,T_1',\lambda_e)]^2 \\ & \quad + \frac{1}{2}Nk(2\lambda_e^2+\lambda_e^{-4}-3) \end{aligned}$$

$$\begin{aligned} \Delta S_2 & = S_2 - S_3 \\ & = \frac{\lambda_e^{-4}}{2[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]}\alpha[f(E_2,T_2',\lambda_e)]^2 \\ & \quad + \frac{1}{2}Nk(2\lambda_e^2+\lambda_e^{-4}-3) \end{aligned}$$

The work is

$$\begin{aligned} \Delta W & = T_2'\Delta S_2 - T_1'\Delta S_1 \\ & = \frac{(T_2'-T_1')}{2}\{[Nk(2\lambda_e^2+\lambda_e^{-4}-3)] \\ & \quad + \frac{\alpha\lambda_e^{-4}}{[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^2+\lambda_e^{-2}-3)]} \\ & \quad \times\{[f(E_2,T_2',\lambda_e)]^2 - [f(E_2,T_1',\lambda_e)]^2\}\} \end{aligned} \tag{83}$$

and the heat absorbed from the outside is

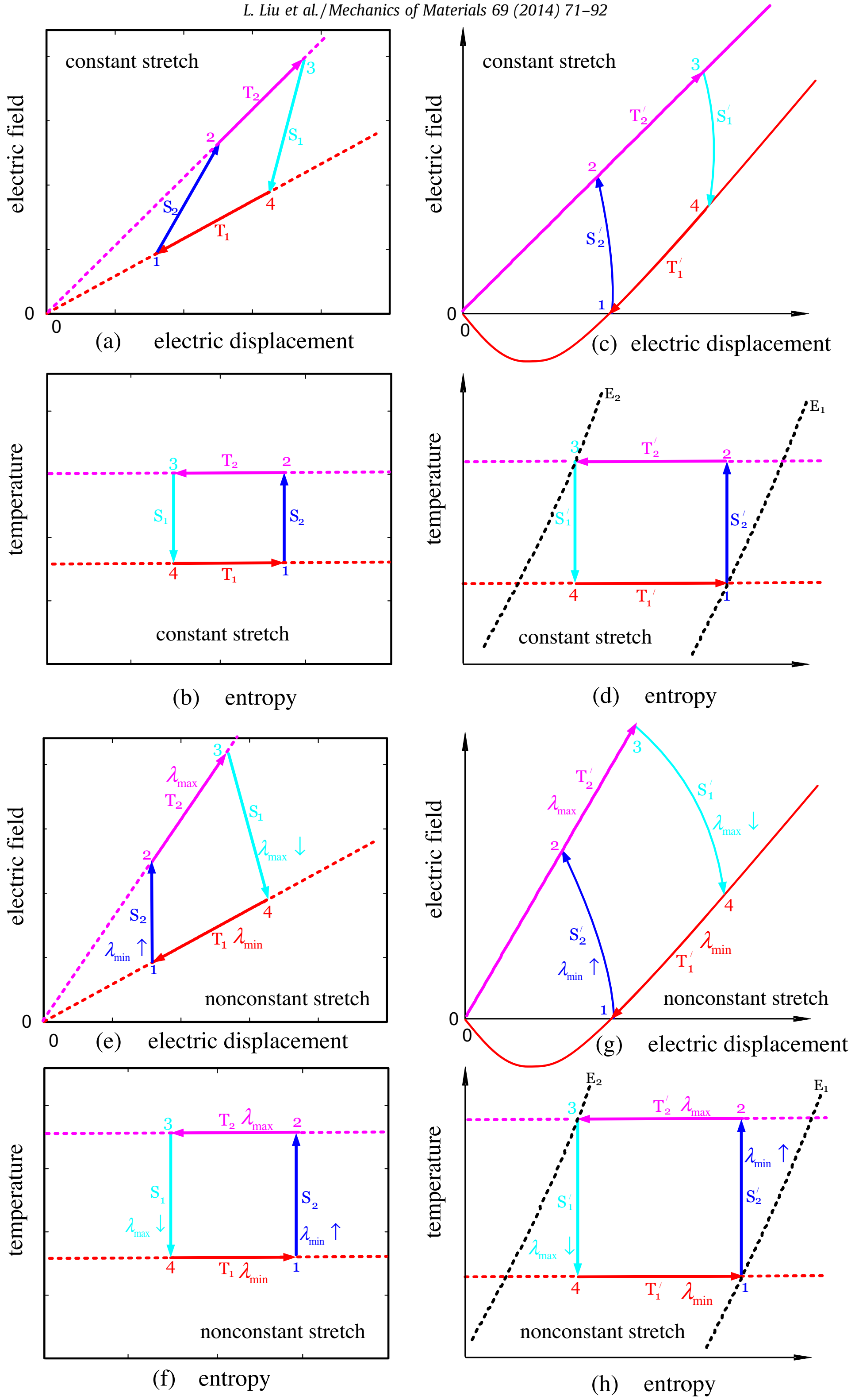


Fig. 11. Working cycle similar to Carnot of polar electric dielectric as cooling devices (a) electric field–displacement plan under constant stretch in ferroelectric phase (b) entropy–temperature plan under constant stretch in ferroelectric phase, (c) electric field–displacement plan under constant stretch undergoing ferroelectric–paraelectric phase transition (d) entropy–temperature plan under constant stretch undergoing ferroelectric–paraelectric phase transition, (e) electric field–displacement plan under nonconstant stretch in ferroelectric phase (f) electric field–displacement plan under nonconstant stretch undergoing ferroelectric–paraelectric phase transition (g) entropy–temperature plan under nonconstant stretch undergoing ferroelectric–paraelectric phase transition.

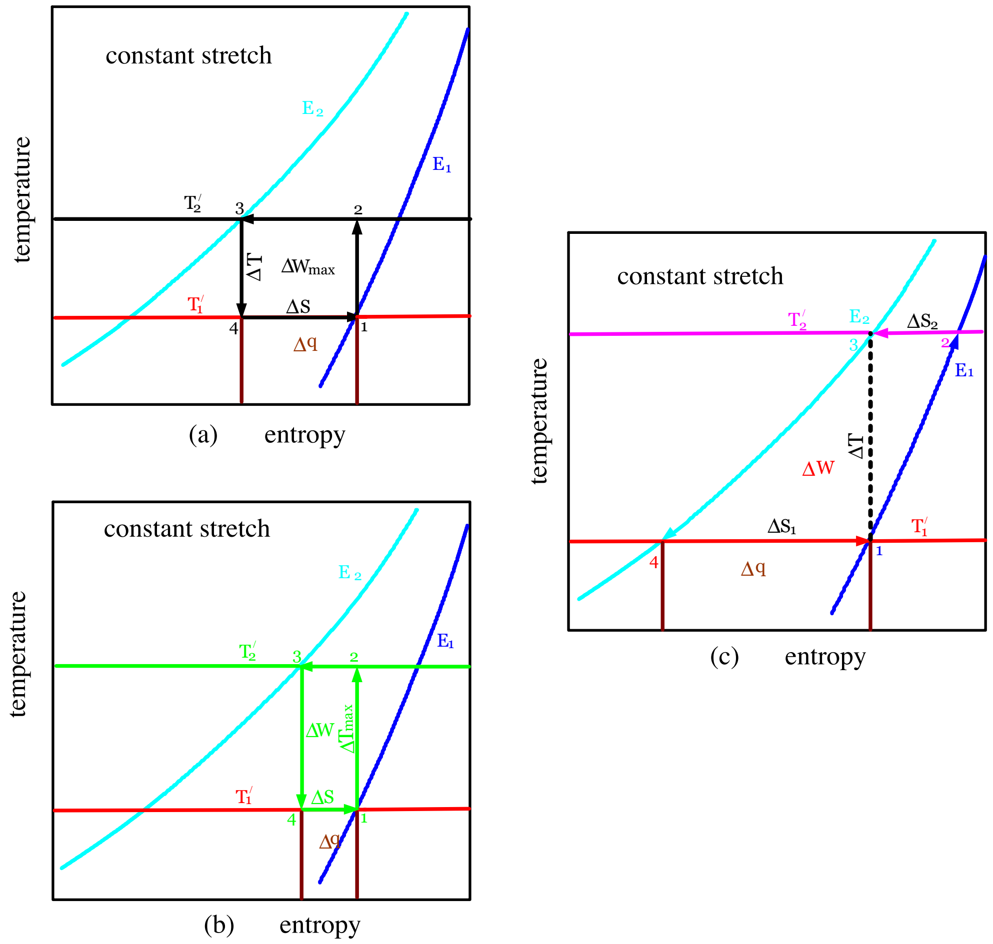


Fig. 12. Several typical thermodynamic cycles of the polar elastic dielectric as cooling devices under constant stretch undergoing ferroelectric–paraelectric phase transition.

$$\Delta q=\left\{\frac{\lambda_e^{-4}}{2[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^{2}+\lambda_e^{-2}-3)]}\alpha[f(E_2,T_1',\lambda_e)]^2+\frac{1}{2}Nk(2\lambda_e^{2}+\lambda_e^{-4}-3)\right\}T_1' \qquad (84)$$

8.4. Polar elastic dielectric as generator undergoing ferroelectric–paraelectric phase transition

In Fig. 13, the working cycle similar to Carnot of polar electric dielectric as generators is demonstrated under different conditions: constant stretch condition, nonconstant stretch condition, undergoing ferroelectric phase and undergoing ferroelectric–paraelectric phase transition. It could be found from the figure that the allowable area is larger in polar electric dielectric undergoing large deformation and phase transition, indicating that the working material after experiencing these two processes may exhibit more obvious ECE, which is more suitable for the fabrication of generators featuring excellent performance.

According to Eq. (80), we could derive the relation between the true electric field and true electric displacement as following:

$$E=\frac{\lambda_e^{-8}}{[1+a(\lambda_e^{-2}-1)+b(2\lambda_e^{2}+\lambda_e^{-2}-3)]}\alpha(T-T_C)D+\xi\lambda_e^{-16}D^3 \qquad (85)$$

When $T_1'<T_C$, considering the polar dielectric generators going through similar Otto thermodynamic cycle of maximal work, the electric quantity could be calculated by using the following equation: point (1) in Fig. 14(c),

$$\frac{\Phi_1}{L_3}=\frac{\lambda_{1e}^{-8}}{[1+a(\lambda_{1e}^{-2}-1)+b(2\lambda_{1e}^{2}+\lambda_{1e}^{-2}-3)]}\alpha(T_1-T_C)\frac{Q_1}{L_1L_2}+\xi\lambda_{1e}^{-16}\frac{Q_1^3}{L_1^3L_2^3}$$

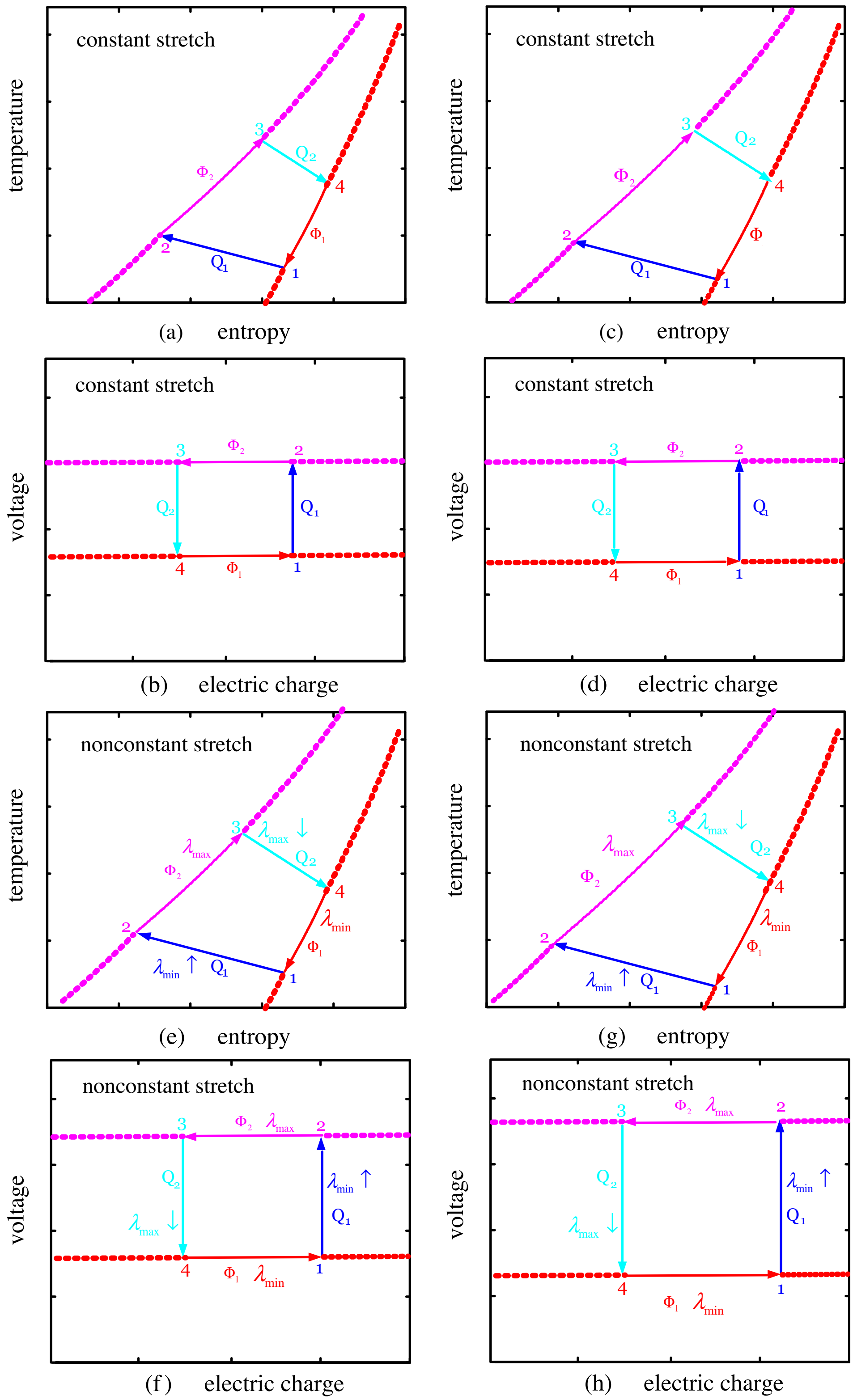


Fig. 13. Working cycle similar to Carnot of polar electric dielectric as generators (a) electric field–displacement plan under constant stretch in ferroelectric phase (b) entropy–temperature plan under constant stretch in ferroelectric phase, (c) electric field–displacement plan under constant stretch undergoing ferroelectric–paraelectric phase transition (d) entropy–temperature plan under constant stretch undergoing ferroelectric–paraelectric phase transition, (e) electric field–displacement plan under nonconstant stretch in ferroelectric phase (f) electric field–displacement plan under nonconstant stretch undergoing ferroelectric–paraelectric phase transition (g) entropy–temperature plan under nonconstant stretch undergoing ferroelectric–paraelectric phase transition.

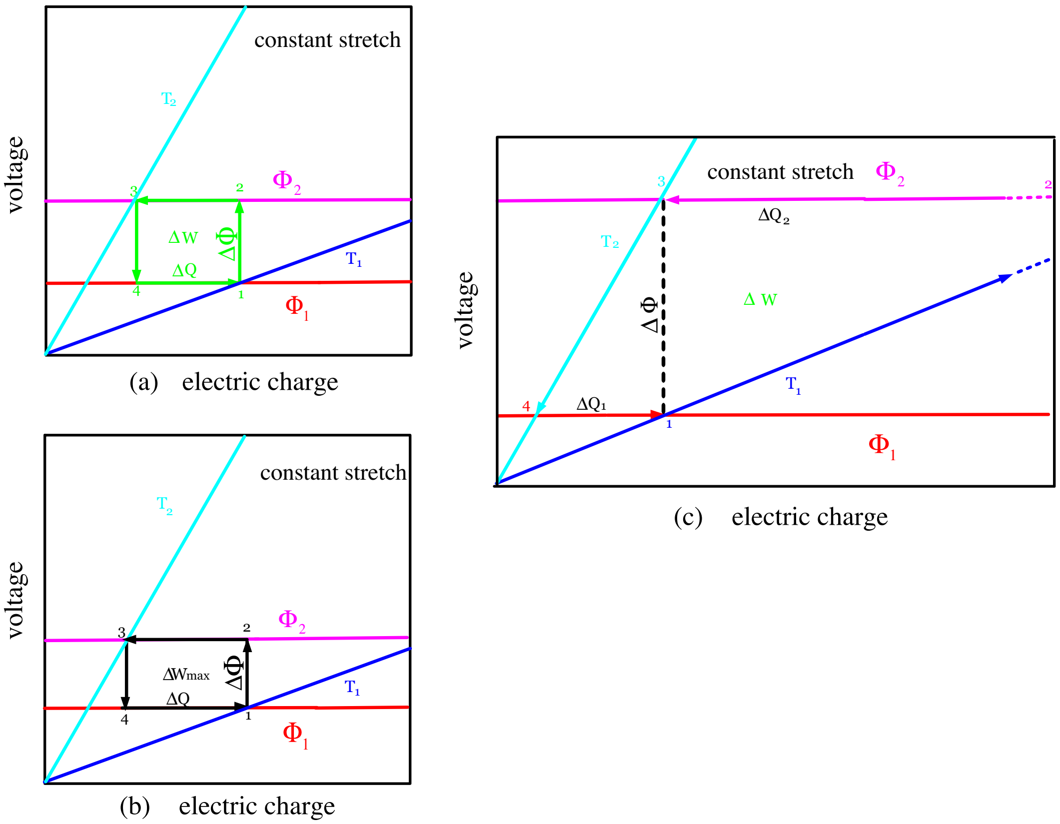


Fig. 14. Several typical thermodynamic cycles of the polar elastic dielectric as generators under nonconstant stretch undergoing ferroelectric–paraelectric phase transition.

point (3),

$$\frac{\Phi_2}{L_3}=\frac{\lambda_{2e}^{-8}}{[1+a(\lambda_{2e}^{-2}-1)+b(2\lambda_{2e}^{2}+\lambda_{2e}^{-2}-3)]}\alpha(T_2-T_C)\frac{Q_3}{L_1L_2}+\xi\lambda_{2e}^{-16}\frac{Q_3^3}{L_1^3L_2^3}$$

here, λ_{e1} and λ_{e2} represent the iso-biaxial deformation of the polar dielectric under the voltage of Φ_1 and Φ_2. L_1, L_2 and L_3 donate the dimension of the generator in the three principal directions. According to $Q_1 = Q_3$, we obtain,

$$\frac{\Phi_2}{\Phi_1}=\frac{\frac{\lambda_{2e}^{-8}}{[1+a(\lambda_{2e}^{-2}-1)+b(2\lambda_{2e}^{2}+\lambda_{2e}^{-2}-3)]}\alpha(T_2-T_C)+\xi\lambda_{2e}^{-16}\frac{Q_1^2}{L_1^2L_2^2}}{\frac{\lambda_{1e}^{-8}}{[1+a(\lambda_{1e}^{-2}-1)+b(2\lambda_{1e}^{2}+\lambda_{1e}^{-2}-3)]}\alpha(T_1-T_C)+\xi\lambda_{1e}^{-16}\frac{Q_1^2}{L_1^2L_2^2}} \tag{86}$$

Therefore, $\Delta\Phi_{\max}=f(T_2, T_1, \lambda_{e2}, \lambda_{e1}, Q_1)$. Point (2),

$$\frac{\Phi_2}{L_3}=\frac{\lambda_{2e}^{-8}}{[1+a(\lambda_{2e}^{-2}-1)+b(2\lambda_{2e}^{2}+\lambda_{2e}^{-2}-3)]}\alpha(T_1-T_C)\frac{Q_2}{L_1L_2}+\xi\lambda_{2e}^{-16}\frac{Q_2^3}{L_1^3L_2^3}$$

point (4),

$$\frac{\Phi_1}{L_3}=\frac{\lambda_{1e}^{-8}}{[1+a(\lambda_{1e}^{-2}-1)+b(2\lambda_{1e}^{2}+\lambda_{1e}^{-2}-3)]}\alpha(T_2-T_C)\frac{Q_4}{L_1L_2}+\xi\lambda_{1e}^{-16}\frac{Q_4^3}{L_1^3L_2^3}$$

In Fig. 14(c),

$$\xi\lambda_{1e}^{-16}\left(\frac{Q_1^3}{L_1^3L_2^3}-\frac{Q_4^3}{L_1^3L_2^3}\right)+\frac{\lambda_{1e}^{-8}}{[1+a(\lambda_{1e}^{-2}-1)+b(2\lambda_{1e}^{2}+\lambda_{1e}^{-2}-3)]}\alpha\left[(T_1-T_C)\frac{Q_1}{L_1L_2}-(T_2-T_C)\frac{Q_4}{L_1L_2}\right]=0$$

According to the above equations we have $\Delta Q_1 = Q_1 - Q_4$. Similarly, we can obtain $\Delta Q_2 = Q_2 - Q_3$ based on the following expression:

$$\xi\lambda_{2e}^{-16}\left(\frac{Q_2^3}{L_1^3L_2^3}-\frac{Q_3^3}{L_1^3L_2^3}\right)+\frac{\lambda_{2e}^{-8}}{[1+a(\lambda_{2e}^{-2}-1)+b(2\lambda_{2e}^{2}+\lambda_{2e}^{-2}-3)]}\alpha\left[(T_1-T_C)\frac{Q_2}{L_1L_2}-(T_2-T_C)\frac{Q_3}{L_1L_2}\right]=0$$

After further calculation, we can obtain the work $\Delta W = \Phi_2\Delta Q_2 - \Phi_1\Delta Q_1$. The work is $\Delta W = \Phi_2\Delta Q_2 - \Phi_1\Delta Q_1$. According to the above mentioned studies, the energy collected by the polar dielectric based energy generator could be expressed as $\Phi_1\Delta Q_1$.

9. Conclusions

A thermodynamic theory of the polar elastic dielectric with a large electrocaloric effect (ECE) and a large deformation capability is proposed in this paper, which describes the condition of equilibrium of the polar elastic dielectric that is subjected to mechanical forces, electric field and thermal field. To analyze the mechanical behavior and large deformation of the polar elastic dielectric thermo-electro-mechanical system, the coupling influence of hyperelastic, polarization, electrostriction and thermal contribution on the system is taken into consideration. We describe the typical thermodynamics cycles of the polar elastic dielectric as cooling devices and energy generators and the electrocaloric and pyroelectric energy conversion are calculated. As an important category of electroactive polymers, ferroelectric polymer is a typical polar dielectric with a large ECE and a large deformation. When ferroelectric polymer is subjected to different voltage, we calculate the temperature change, entropy change, heat absorption and work of the ferroelectric polymer which is regarded as cooling devices. When ferroelectric polymer is subjected to different temperatures, we also calculate the voltage change, electric quantity change and work of the ferroelectric polymer which is regarded as energy generators. The thermo-electro-mechanical coupling behavior of the ferroelectric polymer undergoing ferroelectric–paraelectric phase transition is investigated finally.

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