

Stability of polarization vortices within two interacting ferroelectric nanoparticles

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Abstract

The state of polarization vortices within a ferroelectric nanoparticle could be affected by the long-range electrostatic and elastic interactions from the neighboring particles. Phase field simulations were conducted to investigate the stability of polarization vortices within two interacting ferroelectric nanodots embedded in a non-ferroelectric medium. The interaction between these two nanodots can be neglected if the intermediate distance is larger than a critical distance, whereas the interaction becomes visible once the distance is smaller than that. Two separate vortices were observed to merge into one single vortex once an extreme state of perfect contact condition has been virtually achieved.

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Ever since the concept of toroid moment order in low-dimensional ferroelectric nanostructures was brought forward by first-principles-derived simulations [1], there has been great interest in its potential applications to next generation high density data storage technologies [1-3]. It's been observed numerically and experimentally that non-uniform vortex states of polarizations tend to form in finite-size ferroelectrics [1, 4-7] i.e., nanodots, nanodisks, nanorods, nanowires, etc, to reduce the depolarization energy. Such bistable vortex states of polarization are switchable [8-10], and therefore could be used to represent binary signals in ultra-high density data storage devices that consist of dielectric mediums with series of embedded nanoscale ferroelectric units.

Although the number of experimental reports is still limited, theoretical investigations on the dynamics of vortex polarization states have been carried out through different approaches, such as first-principles-derived effective Hamiltonian methods [1], first-principles density-functional-theory-based methods [5], and Ginzburg-Landau-theory-based phenomenological approaches [4]. It's been observed that the configurations of the polarization vortex states are highly dependent on certain factors, such as the nanostructure size [4, 11], the long range interactions [12], the intrinsic surface tension [13], and specific electromechanical boundary conditions [8, 14].

Among many fundamental problems, the stability of single polarization vortex state within a ferroelectric nanoparticle is of great importance to the design of related high density data storage devices. For instance, a memory system can be designed to consist of organized ferroelectric nanodots that are embedded in a non-ferroelectric medium, e.g., a dielectric thin film. The capacity of such system depends on the average space between each embedded ferroelectric

unit. Since the possibility exists for polarization vortex state in each nanodot to be affected by the long-range electrostatic and elastic interactions from the neighboring units, one needs to understand the mechanism of interaction between adjacent ferroelectric nanoparticles to assure the stability of the vortex structures within.

In this letter, the stability of vortex structures of polarization due to the interaction between adjacent ferroelectric nanodots was numerically investigated. We consider two separate ferroelectric nanodots, with a certain distance from each other, that are embedded in a non-ferroelectric medium. In order to study the effects on the stability of polarization vortex brought by the interaction between these two nanodots, a phenomenological phase field approach has been employed to conduct three-dimensional (3D) simulations on the dynamics of polarization states within the system. In this phase field approach, the components of spontaneous polarization P_i are taken to be the order parameters. The total free energy of the system takes the form of $F(\varepsilon_{ij}, E_i, P_i, P_{i,j})$, where ε_{ij} ($i, j=1, 2, 3$) are the components of strain tensor, E_i the components of electric field vector, and the subscript “, j” represents partial differentiation with respect to the x_j coordinate direction. The temporal evolution of the polarization can be calculated from the following time-dependent Ginzburg–Landau equation

$$\frac{\partial P_i(\mathbf{r}, t)}{\partial t} = -L \frac{\delta F}{\delta P_i(\mathbf{r}, t)} \quad (i=1, 2, 3) \quad , \quad (1)$$

where L is the kinetic coefficient, $\delta F / \delta P_i(\mathbf{r}, t)$ represents the thermodynamic driving force for the spatial and temporal evolutions of the simulated system, \mathbf{r} denotes the spatial vector $\mathbf{r} = (x_1, x_2, x_3)$, and t is time. The total free energy F can be generally expressed as [15, 16]

$$F = \int_V [f_{\text{Lan}}(P_i) + f_{\text{grad}}(P_{i,j}) + f_{\text{elas}}(\varepsilon_{ij}, P_i) + f_{\text{elec}}(E_i, P_i)] dV \quad , \quad (2)$$

where f_{Land} is the Landau free energy density, f_{grad} is the gradient energy density that gives the energy penalty for spatially inhomogeneous polarization, f_{elas} denotes the elastic energy density, and f_{elec} represents the self-electrostatic energy density. A detailed description for the terms of free energy in Eq. (2) and the related coefficients can be found in Ref. [4, 15]. In addition to Eq. (1), the mechanical equilibrium equation $\sigma_{ji,j} = 0$ and the electrostatic equilibrium equation $\varepsilon_0(\kappa_{11}\partial^2\varphi / \partial x_1^2 + \kappa_{22}\partial^2\varphi / \partial x_2^2 + \kappa_{33}\partial^2\varphi / \partial x_3^2) = \partial P_1 / \partial x_1 + \partial P_2 / \partial x_2 + \partial P_3 / \partial x_3$ must be satisfied for a given polarization distribution, where σ_{ij} are the components of stress, φ the electrostatic potential, ε_0 the dielectric constant of vacuum and κ_{ij} the components of relative dielectric constants of the material. The mechanical equilibrium equation can be solved analytically by employing the general eigenstrain theory for a given polarization distribution under the periodic boundary condition [15, 17]. The electrostatic potential is obtained by solving the electrostatic equilibrium equation [16]. In the electrostatic equilibrium equation, by assuming $\kappa_{ij} = 0$ when $i \neq j$, the relative dielectric constant matrix is diagonal [16]. This model is good for isothermal process below the Curie temperature only, and needs to be extended if temperature dependence is considered. The charge compensation is not considered in this work because the ferroelectric nanoparticles are embedded in an electrically insulating medium, corresponding to an ideal open-circuit boundary condition.

In order to investigate the interaction between two adjacent ferroelectric nanodots, a virtual experiment has been conducted through the above mentioned phase field simulation. The size of the overall simulated system, including two ferroelectric dots and the surrounding non-ferroelectric medium, is 128x128x64 discrete grids with a scale of $\Delta x_1 = \Delta x_2 = 0.5\text{nm}$ and $\Delta x_3 = 0.25\text{nm}$. Specifically the size of the dots is 32x32x16 grids each. These two dots, aligned in x_1 direction

with an intermediate surface-to-surface distance of d , are then embedded in the non-ferroelectric medium. Periodic boundary conditions are set in all three directions for the outer boundaries of the surrounding medium. The interfaces between the ferroelectric nanodots and the surrounding medium are assumed to be coherent. Zero boundary condition, i.e. $\mathbf{P}=0$, is used for spontaneous polarizations at the interfaces. The material constants adopted in the present simulations are the same as those used in Ref [16]. The elastic and dielectric constants of the non-ferroelectric medium are assumed to be the same as those of the ferroelectric nanodots such that the solutions to the mechanical and electrostatic equilibrium equations can be obtained analytically [16, 17]. The semi-implicit Fourier-spectral method [18] is employed to solve Eq. (1). A constant room temperature is assumed throughout the numerical experiment.

Phase field simulation was then conducted on the above mentioned geometric model. One can refer to Ref [4] for typical 2D and 3D polarization distribution in one of the nanodots. It is noticed in Ref [4] that the polarization distribution is x_3 -independent. Therefore our attention is mainly given to the effects on polarizations in x_1 - x_2 plane for all simulation results. Fig. 1(a₁)-(a₂) shows the polarization distribution in x_1 - x_2 plane within two nanodots that are separated by a distance of $d=16\text{nm}$. It is noticed that the toroidal distributions of the polarization remain the same, meaning that the interaction between the two vortices is negligible. But once the distance is gradually decreased, the interaction effect on the vortex structures becomes visible. Fig. 1(b₁)-(b₂) shows such scenario after the distance d is decreased to 4nm. It is observed that the polarization vectors near the far ends of the two dots do not have significant change, whereas the polarizations in the area closer to the adjacent interfaces start to deviate from the original distribution. The P_1 component has an increase at the upper and lower corner of the adjacent

interfaces and the corresponding P_2 component has been significantly reduced. Such changes can be easily identified by looking at the contour plots for P_2 component in Fig. 1(b₁)-(b₂). Once the distance d is further reduced to 1nm, the interaction effect becomes stronger and more obvious as shown in Fig. 1(c₁)-(c₂). For such a tiny gap between the two nanodots, the interaction has significantly affected the polarization distribution in the areas closer to the adjacent interfaces. The polarizations within the affected areas have mostly evolved to be parallel to x_1 direction. The centers of vortices have also shifted to be closer to the adjacent interfaces. To have a closer look at the polarization distribution near the interacting interfaces, the P_1 component of polarization in the left dot along its right interface has been plotted in Fig. 2 for different intermediate distances from 0 to 48nm. It's been observed that the values of P_1 are antisymmetric about the centerline parallel to x_1 direction, and the magnitude increases as the two dots are getting closer. No visible change of P_1 is observed once the distance is greater than 16nm. The normalized toroidal moment G of the dots are plotted as a function of the normalized intermediate distance in Fig. 3. It is noticed that the magnitude of G has an apparent change once the distance is less than 16nm. Fig. 2 and Fig.3 together demonstrated that the vortex structures are not stable once two separate ferroelectric nanodots get close enough to each other, and the critical distance is around 16nm, which is equivalent to the dimension of a single dot. The long-range (or nonlocal) electrostatic and elastic interactions of spontaneous polarizations and strains will cause significant interaction between the adjacent nanodots via the non-ferroelectric medium.

It is imaginable that the interaction will get even stronger once the two dots are positioned even closer. One extreme case would be that the two adjacent dots are in perfect contact and the intermediate gap vanishes. To demonstrate the states of polarization vortices within two nanodots

in perfect contact, these nanodots are virtually positioned together without intermediate dielectrics in between. Each nanodot possesses its own vortex structure of polarizations at the initial stage as shown in Fig. 4(a). It is noticed that 180° polarization jump exists at the interface area. Such configuration is of course not stable and will relax during the following computing steps as shown in Fig. 4(b) and Fig. 4(c) until an equilibrium state is reached as shown in Fig. 4(d). It's been noticed through Fig. 4(a)-(c) that the double-vortex configuration will gradually evolve to a single-vortex structure, which has been discussed in Ref [11]. According to the computational results in Fig. 4, one understands that the contact of two ferroelectric nanodots might cause the vortex structure in each individual dot to disappear, leading to loss of data during the application of data storage. It should be noted as well that the transfer from double-vortex to single-vortex configuration happens only if the vortices are in the same vortical directions at the initial stage. If the vortical directions are different, then a double vortex configuration will remain in the nanodots that are in perfect contact. This is because a double-vortex configuration with opposite vortical directions is energetically favored, and will remain stable in the system [11].

In summary, phase field simulation has been conducted to investigate the interaction of two ferroelectric nanodots that are embedded in a non-ferroelectric medium. It's been shown in this letter that the interaction between two adjacent dots will affect the stability of polarization distribution within. Via the intermediate dielectrics, the long-range electrostatic and elastic interactions of spontaneous polarizations and strains will cause deviations of the polarizations in the nanodots from the original vortex distribution near the adjacent interfaces. The strength of such effect is depending on the intermediate distance between the dots. A critical distance of 32-grid (equivalent to the dimension of a single dot) is determined from the computational results.

The interaction can be neglected when the distance is larger than the critical distance, whereas the interaction effect becomes stronger and more visible as the intermediate distance decreases below the critical distance. Finally, a perfect contact condition has been achieved by virtually positioning the two nanodots together without intermediate dielectrics. It's been observed from the simulation results that the double-vortex configuration, with the same vortical direction, is not stable in the double-dot-in-contact system and will eventually evolve to a squeezed single-vortex structure. The simulation results presented in this letter suggest that the interactions among nanoscale ferroelectric units should be carefully considered while designing ferroelectric nanostructure reinforced data storage devices, and contact between adjacent functional units should be highly prohibited.

Acknowledgements

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List of Figure Captions

1. The steady states of the vortices within two adjacent nanodots with different intermediate distances: (a₁)-(a₂) d=16nm; (b₁)-(b₂) d=4nm; and (c₁)-(c₂) d=1nm (The subscripts 1 and 2 denote the left and right dots, respectively). The contour plots indicate values of normalized polarization component P₂. The characteristic polarization is set as P₀=0.757 Cm⁻².
2. The normalized polarization component P₁ along the right surface of the left dot in the double-dot system for different intermediate distances from 0 to 48 nm. The characteristic length is set as x₀=0.5 nm.
3. The normalized toroidal moment G of the dots for different intermediate distances dx₁. The toroidal moment of polarization is defined as $\mathbf{G} = \frac{1}{V} \int_V \mathbf{r} \times \mathbf{P} dV$. The characteristic moment is defined as G₀=r₀P₀=1nm×0.757C/m²=0.47e/Å, in which r₀ and P₀ are the duple characteristic length and the characteristic polarization, respectively.
4. The dynamics of the vortex structures within two nanodots that are in perfect contact: (a) Initial state; (b) the state after 600 time steps; (c) the state after 800 time steps; and (d) the final state in equilibrium where two vortices merge into one single-vortex structure. The contour plots indicate values of normalized polarization component P₁.

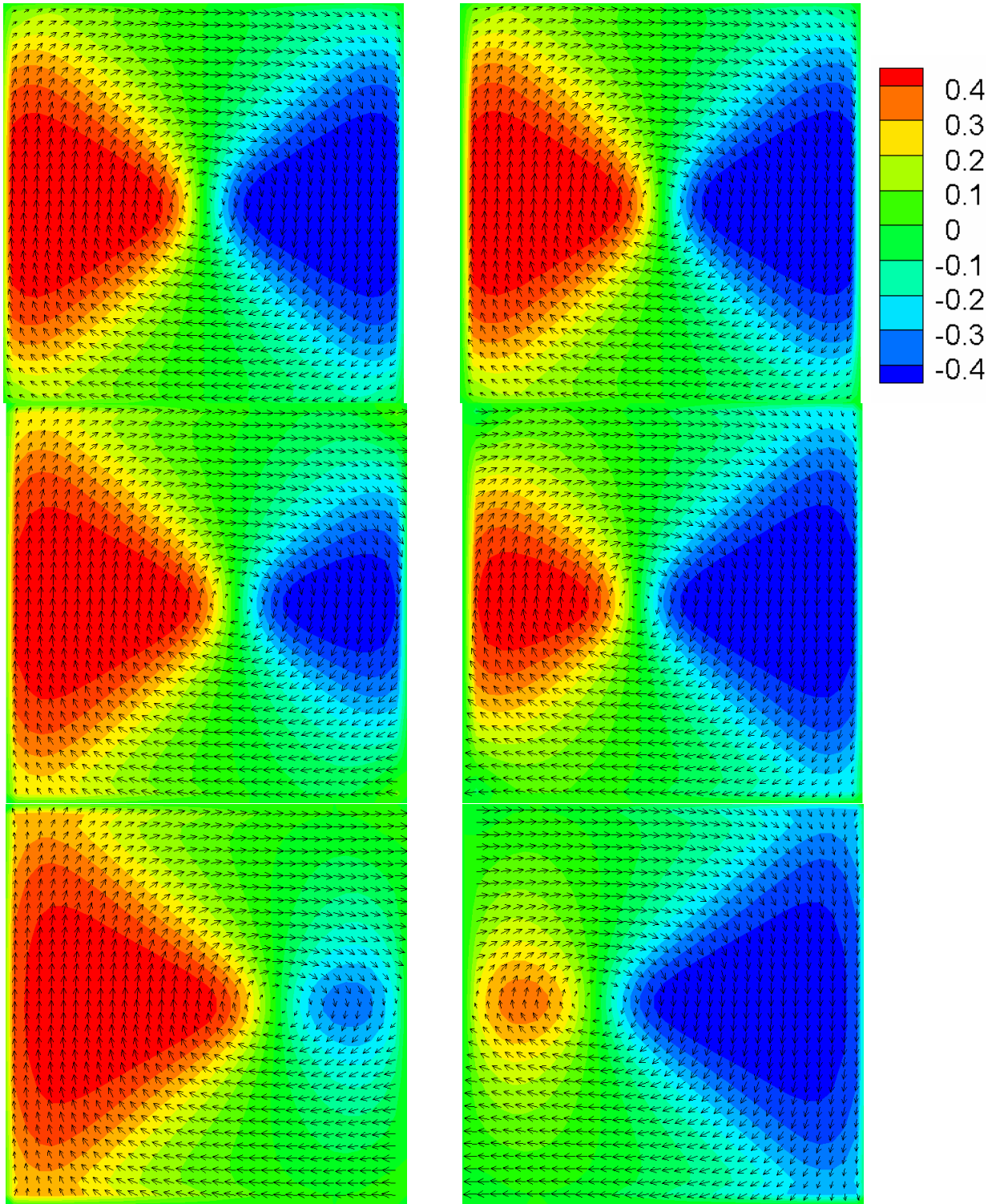


Fig. 1

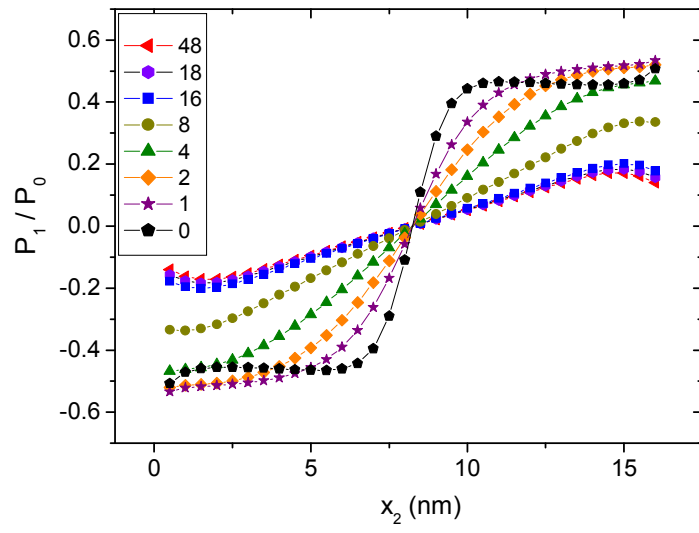


Fig. 2

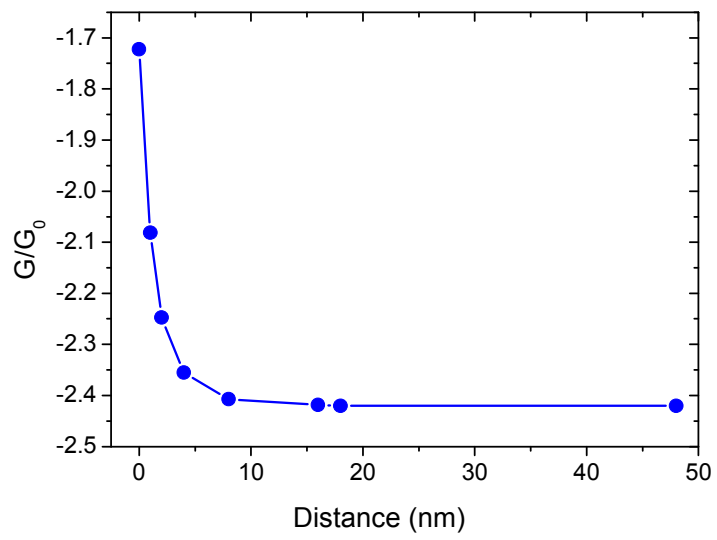


Fig. 3

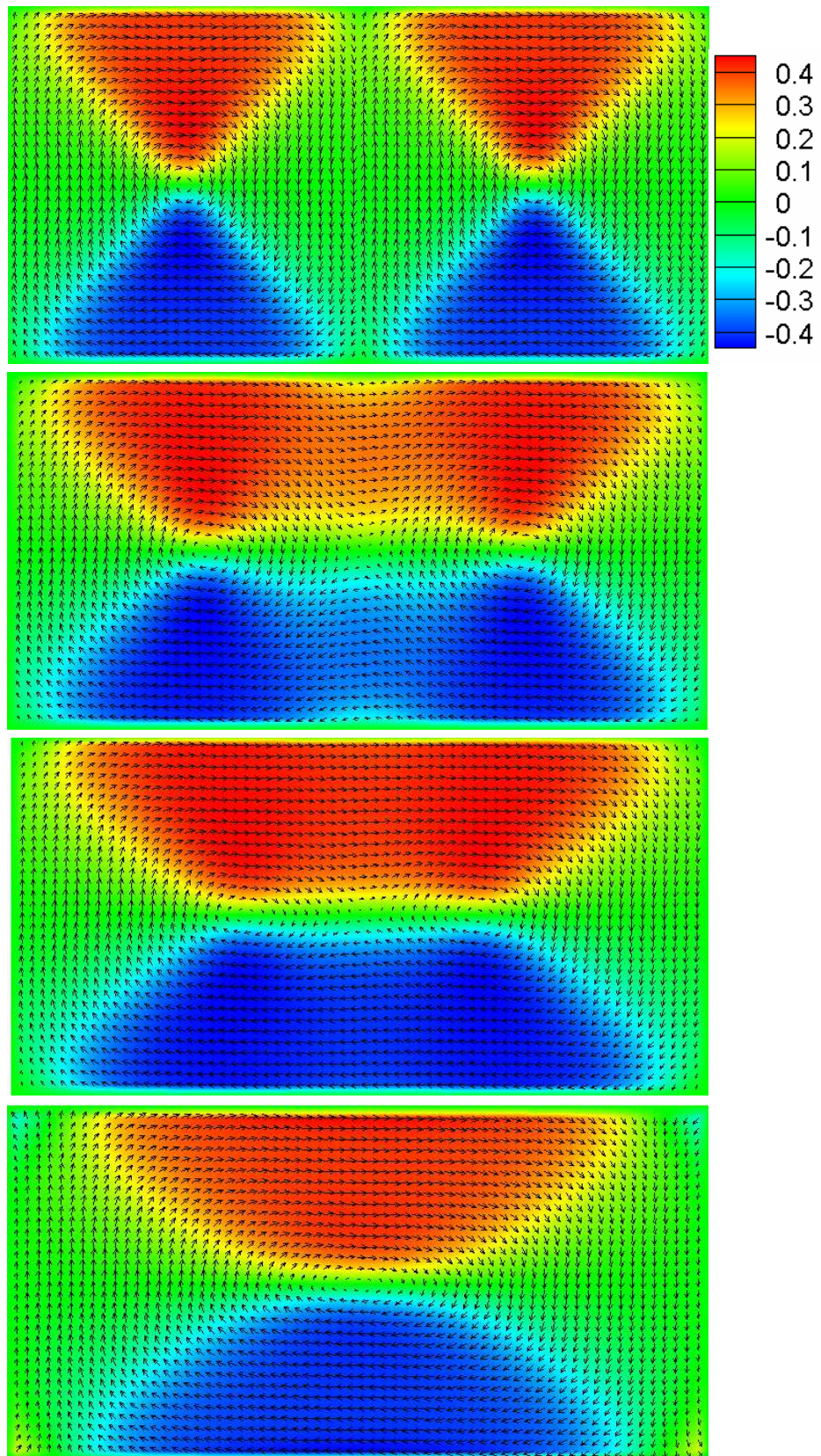


Fig. 4