Monte Carlo simulation of polarization switching and electrocaloric effect in ferroelectrics with random fields

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Motivation

- *Electrocaloric effect* (ECE) has high application potential for solid refrigeration.
- Some *relaxor ferroelectrics* (RFEs) can produce higher ECE at lower electric field.
- Origins of RFEs and ECE are still under debate, and are deserved to be studied and optimized.

Lattice based model

Lattice based model is utilized for calculation with periodic boundary condition. Lattice constant $a_0 = 4$Å, and thus the volume of unit cell $V_0 = a_0^3$.

Total energy

$$H^* = H_D + H_{dip} + H_{gr} + H_e + U$$

Landau multi-well potential:

$$H_D = V_0 \sum_i \Big[-\frac{a}{2}(P_x^2(\mathbf{r}_i) + P_y^2(\mathbf{r}_i)) + \frac{b}{4}(P_x^4(\mathbf{r}_i) + P_y^4(\mathbf{r}_i)) \Big]$$

where $a = 13.7128 \times 10^8 \mathrm{J\,m\,C^{-2}}$, $b = 28.908 \times 10^9 \mathrm{J\,m^5\,C^{-4}}$, $\mathbf{r}_i$ is the coordinate of site i.

Dipole-dipole interaction energy:

$$H_{dip} = S_A V_0^2 \frac{1}{8\pi\epsilon_0\epsilon_r} \sum_{[i,j]} \Big[\frac{\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{P}(\mathbf{r}_j)}{|\mathbf{r}_{ij}|^3} - \frac{3[\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{r}_{ij}][\mathbf{P}(\mathbf{r}_j)\cdot\mathbf{r}_{ij}]}{|\mathbf{r}_{ij}|^5} \Big]$$

where $\epsilon_r = 12$ is the relative permittivity at high frequency and the cut-off radius is eight times the lattice constant.

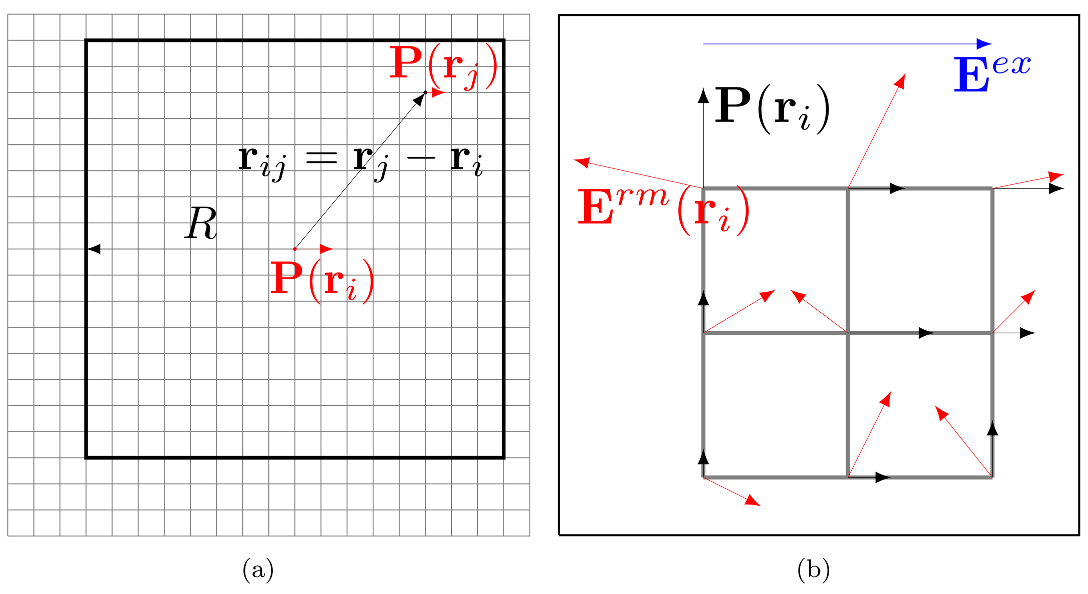

FIGURE 1: *Illustration for (a) dipole-dipole interaction and (b) electrostatic energy.*

Gradient energy:

$$H_{gr} = S_J V_0 \sum_i \Big[g_1(P_{x,x}^2(\mathbf{r}_i) + P_{y,y}^2(\mathbf{r}_i)) + g_1' P_{x,x}(\mathbf{r}_i)P_{y,y}(\mathbf{r}_i) + g_2(P_{x,y}(\mathbf{r}_i) + P_{y,x}(\mathbf{r}_i))^2 + g_2'(P_{x,y}(\mathbf{r}_i) - P_{y,x}(\mathbf{r}_i))^2 \Big]$$

where $P_{i,j} = \partial P_i / \partial x_j$ and $g_1 = g_1' = g_2 = g_2' = 2 \times 10^{-11}\,\mathrm{J\,m^3\,C^{-2}}$.

Electrostatic energy:

$$H_e = -V_0 \sum_i \Big[\mathbf{P}(\mathbf{r}_i) \cdot (\mathbf{E}^{ex} + \mathbf{E}^{rm}(\mathbf{r}_i)) \Big]$$

where $\mathbf{E}^{ex}$ is the external electric field, $\mathbf{E}^{rm}(\mathbf{r}_i)$ is the random field[1] at site i.

Thermal energy:

$$U = \frac{f}{2} N k_B T$$

where f is the number of degrees of freedom per unit cell, N is the number of sites.

Simulation algorithm

Canonical Monte Carlo: $T = constant$.

$$p(\mathbf{r}_i) = min\left[1, \exp\left(-\frac{\Delta H(\mathbf{r}_i)}{k_B T}\right)\right]$$

where $\Delta H(\mathbf{r}_i)$ denotes the change in the potential energy of the system. The switching is approved if the switching probability $p(\mathbf{r}_i)$ for site i is not less than a randomly generated number Rnd within $[0,1]$.

Microcanonical Monte Carlo[2]: $H = constant$.

$$\sum_{i,k} Demon(\mathbf{r}_i, k) = \frac{f}{2} N k_B T$$

where $Demon(\mathbf{r}_i, k)$ is the thermal energy at site i for the k-th demon. If $\Delta H(\mathbf{r}_i)$ is not less than $Demon(\mathbf{r}_i, k)$, the switching is approved, and $Demon(\mathbf{r}_i, k) = Demon(\mathbf{r}_i, k) - \Delta H(\mathbf{r}_i)$.

Results

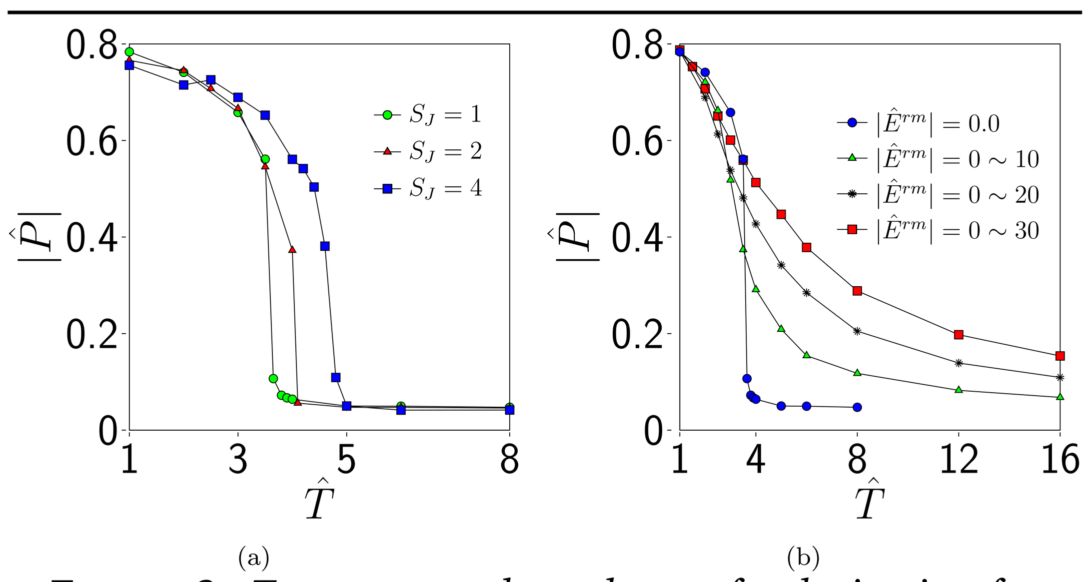

FIGURE 2: *Temperature dependence of polarization for (a) ferroelectrics (FEs) with $S_A = 1$, $|\hat{E}^{rm}| = 0$ and (b) RFEs with $S_A = 1$, $S_J = 1$. $T = T_0\hat{T}$, $T_0 = 100$ K; $P = P_0\hat{P}$, $P_0 = 0.46$ Cm^{-2}.*

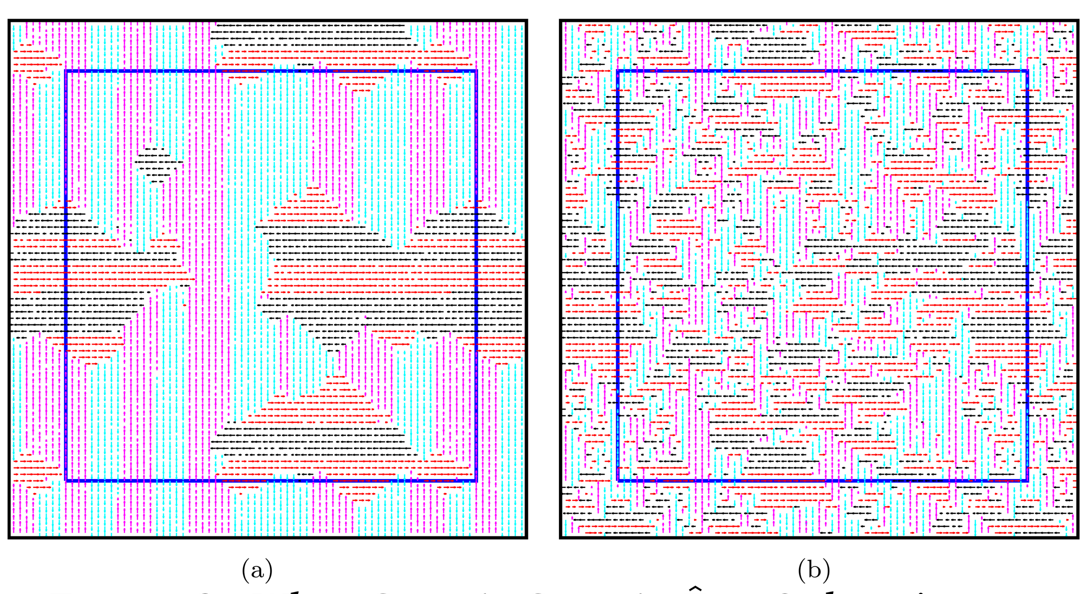

FIGURE 3: *When $S_A = 1$, $S_J = 1$, $\hat{T} = 2$ domain configurations are illustrated for (a) FEs and (b) RFEs with $|\hat{E}^{rm}| = 20$. $E = E_0\hat{E}$, $E_0 = 4.6875 \times 10^7$ Vm^{-1}.*

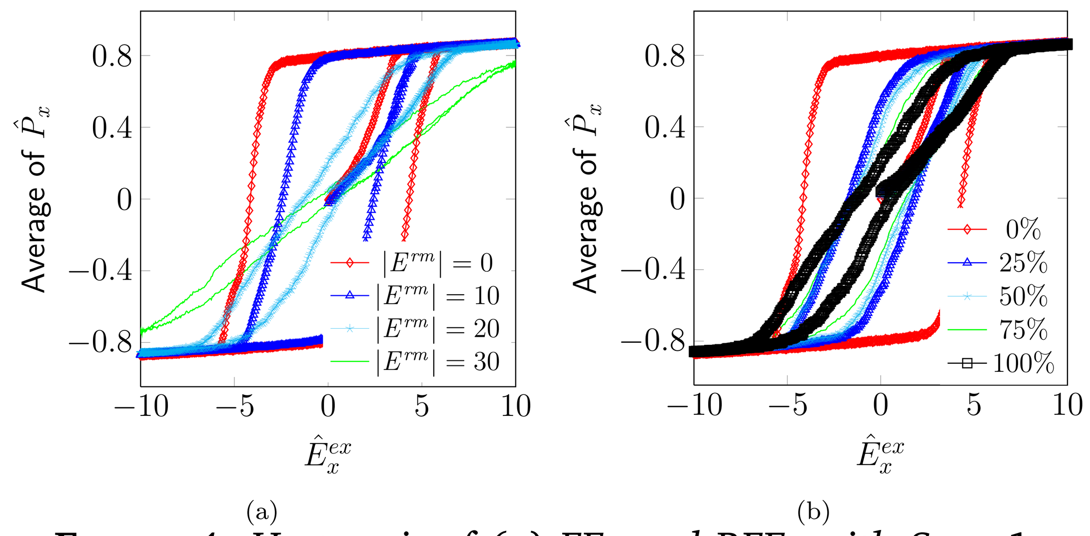

FIGURE 4: *Hysteresis of (a) FEs and RFEs with $S_J = 1$, $S_A = 1$, $\hat{T} = 2$ and (b) RFEs with $|\hat{E}^{rm}| = 20$ for different proportions of sites with random fields.*

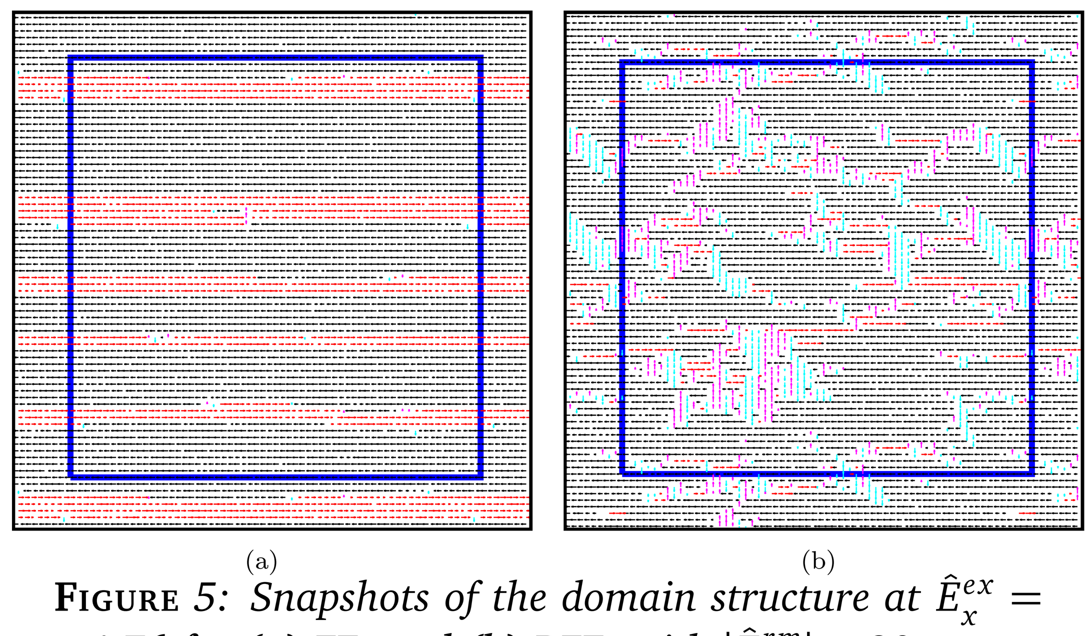

FIGURE 5: *Snapshots of the domain structure at $\hat{E}_x^{ex} = -4.76$ for (a) FEs and (b) RFEs with $|\hat{E}^{rm}| = 20$.*

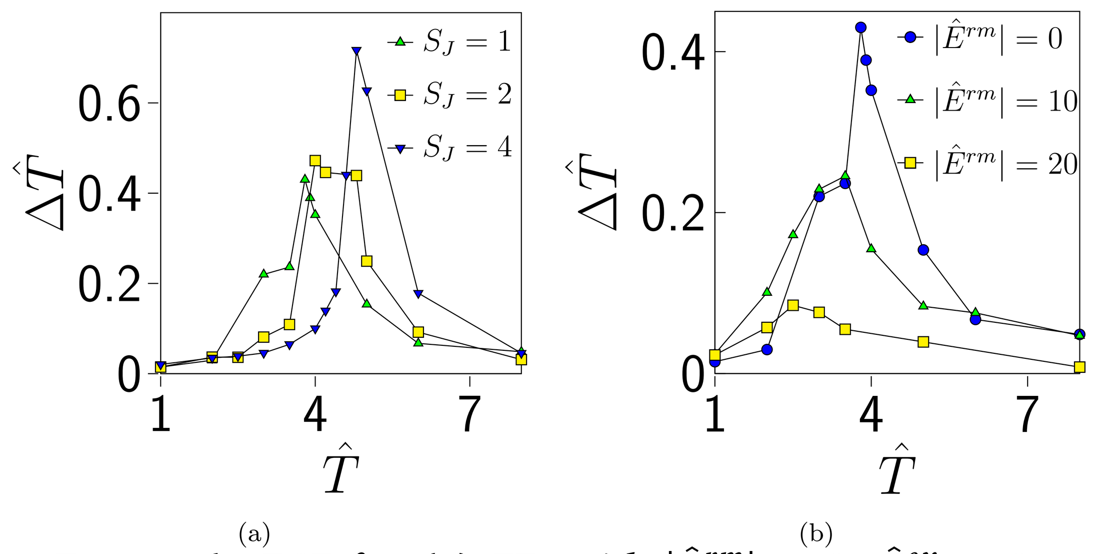

FIGURE 6: *ECE for (a) FEs with $|\hat{E}^{rm}| = 0$, $\hat{E}_x^{ex} = 2$, $S_A = 1$ and (b) RFEs with $S_A = 1$, $S_J = 1$, $\hat{E}_x^{ex} = 2$.*

Conclusions

- Higher gradient energy leads to higher phase transition temperature. Static random fields result in a wide phase transition range.
- Domain miniaturization and decrease of remnant polarization are observed when random fields are present.
- The magnitude of random fields determines the decrease in the saturation polarization, while the number of random fields is responsible for the decrease of the remnant polarization.
- Gradient energy and dipole interaction promote ECE effect. Higher gradient energy shifts the ECE peak to higher temperature.
- When the random field is stronger, the ECE effect becomes weaker, but the ECE peak is shifted to a lower temperature.

Acknowledgements

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References

[1] V. Westphal, W. Kleemann, and M. D. Glinchuk. Diffuse phase transitions and random-field-induced domain states of the "relaxor" ferroelectric pbmg$_{1/3}$nb$_{2/3}$o$_3$. *Phys. Rev. Lett.*, 68:847–850, Feb 1992.

[2] I. Ponomareva and S. Lisenkov. Bridging the macroscopic and atomistic descriptions of the electrocaloric effect. *Phys. Rev. Lett.*, 108:167604, 2012.