Self-organization into ferroelectric and antiferroelectric crystals via the interplay between particle shape and dipolar interaction

Kyohei Takae^{a,1} and Hajime Tanaka^{a,1}

^aDepartment of Fundamental Engineering, Institute of Industrial Science, University of Tokyo, Tokyo 153-8505, Japan

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Ferroelectricity and antiferroelectricity are widely seen in various types of condensed matter and are of technological significance not only due to their electrical switchability but also due to intriguing cross-coupling effects such as electro-mechanical and electro-caloric effects. The control of the two types of dipolar order has practically been made by changing the ionic radius of a constituent atom or externally applying strain for inorganic crystals and by changing the shape of a molecule for organic crystals. However, the basic physical principle behind such controllability involving crystal–lattice organization is still unknown. On the basis of a physical picture that a competition of dipolar order with another type of order is essential to understand this phenomenon, here we develop a simple model system composed of spheroid-like particles with a permanent dipole, which may capture an essence of this important structural transition in organic systems. In this model, we reveal that energetic frustration between the two types of anisotropic interactions, dipolar and steric interactions, is a key to control not only the phase transition but also the coupling between polarization and strain. Our finding provides a fundamental physical principle for self-organization to a crystal with desired dipolar order and realization of large electro-mechanical effects.

dipolar crystal | ferroelectricity | antiferroelectricity | structural phase transition | mechanical switching

Ferroelectricity and antiferroelectricity are manifestations of long-range dipolar ordering with and without macroscopic polarization, respectively. These phases are widely observed in various materials, such as inorganic oxides (1), organic molecular solids (2), polymers (3), liquid crystals (4), metal–organic frameworks (5), and supramolecular systems (6). Phase transitions between paraelectric, ferroelectric, and antiferroelectric phases are often accompanied by a large change in spontaneous polarization, dielectric permittivity, crystalline structure (lattice strain), and entropy. Because of these intriguing characteristics, they have attracted considerable attention from condensed matter physics (7–10), chemistry (6, 11, 12), and technological applications including nonvolatile memories, electro-mechanical actuators, and electro-caloric refrigerators (13–22).

Typical examples of ferroelectric–antiferroelectric phase transitions in inorganic substances are $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (1) and $(\text{Bi,RE})\text{FeO}_3$ (14, 23), where RE stands for a rare earth metal atom. In these substances, the ionic radius ratio (or the Goldschmidt tolerance factor) is a key factor controlling the phase behavior (23). Interestingly, similar effects arising from the ionic radii of constituent atoms have also been reported for the magnetic analogue, i.e., the emergence of antiferromagnetic phase. It is worth noting that, in some cases, colossal magnetoresistance can be induced by using phase transitions between ferromagnetic and antiferromagnetic phases (24). Another known method to control antiferroelectric transformation is to apply a biaxial epitaxial stress on thin films (14–16). In an epitaxial thin film of PbZrO_3 , for example, strain generated by a lattice mis-

fit to the substrate is known to be a crucial factor determining the crystalline structure and polarization ordering (25, 26), suggesting the importance of electro-mechanical coupling in the phase transition. Examples of antiferroelectric phases can also be seen in molecular crystals (2, 6, 27), organic–inorganic hybrid perovskites (28), and liquid crystals (4) such as benzimidazoles organic crystals (29). For a 1:1 adduct of iodanilic/chloranilic acid with 5,5'-dimethyl-2,2'-bipyridine (55DMBP), for example, ferroelectricity and antiferroelectricity emerge for iodanilic and chloranilic acids, respectively (11, 30). It was also shown that the ferroelectric transition in the former case vanishes at high pressure, while another anomaly in dielectric permittivity remains. Quite recently, furthermore, ferroelectricity was observed in columnar supramolecular crystals of benzene-1,3,5-triamides (BTAs) by controlling steric intermolecular interactions (12).

In all of the above examples, the type of dipolar order is controlled by a certain controlling parameter. In particular, in the organic substances, a key controlling factor is thought to be a molecular shape, although there is no unified physical understanding on how to stabilize each phase by such modifications. Although the key structural factor responsible for the emergence of each of ferroelectric and antiferroelectric ordering has been investigated for individual systems (25, 26, 31–38), the

Significance

Controlling ferroelectricity and antiferroelectricity of a crystalline solid is one of the central issues in material science and technological applications because the dielectric, electromechanical, and thermoelectric properties crucially depend on the type of dipolar order. However, still missing is a simple particle-based physical model that shows self-organization into a lattice structure of desired dipolar order in a controlled manner. Here we elucidate the importance of competition between anisotropic steric and dipolar interactions in such self-organization. We also reveal that the interplay between the two types of anisotropy with different origins is a key to cross-coupling properties of solids such as mechanical switchability of ferroelectric and antiferroelectric phases. These findings will provide a useful guide for designing materials with dipolar order.

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¹To whom correspondence may be addressed. Email: tanaka@iis.u-tokyo.ac.jp or takae@iis.u-tokyo.ac.jp.

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physical origin of the structural phase transition accompanying a crystal–lattice change between the two types of polarization ordering and its coupling to mechanics remain elusive. Furthermore, it is unclear whether there are any common underlying physics behind ferro-to-antiferro ordering seen in a wide class of materials.

As a first step toward the unified understanding of these phenomena, we propose a simple candidate mechanism, which may be relevant for the organic systems: competition between steric and dipolar interactions. To realize this by a simple particle-based model, we construct a system consisting of spheroid-like Lennard-Jones particles with a point dipole, whose shape anisotropy (i.e., the aspect ratio characterized by an anisotropy parameter η) is introduced as a key physical parameter to control the short-range repulsive interaction (*Materials and Methods*). So far there have been many particle-based modelings of ferroelectric ordering (39–44), but no reports on antiferroelectric ordering and phase controllability. Our model may not be universal [e.g., not directly applied to perovskite-type solids where a point dipole moment cannot be well defined even approximately (45)], but captures essential physics behind self-organization of dipoles into two types of long-range dipolar order into different crystalline lattices: competing orderings. Fig. 1*A* schematically shows a key idea of our model: The electric interaction between point dipoles is intrinsically anisotropic, and its sign depends on the particle arrangement (46). Thus, the particle arrangement favored by steric repulsions is not necessarily favored by dipolar interactions. Such frustration is more significant for particles with larger anisotropy η . Thus, the increase of η destabilizes the ferroelectric crystalline lattice structure and results in a structural transition to an antiferroelectric phase with a different lattice structure (Fig. 1*A–D*). In relation to this, it is worth noting that even in simple dipolar systems an interesting hysteretic response is observed under a specially designed arrangement of dipoles (47). In this article, we show a simple physical principle, by which we are able to control the tendency toward ferroelectric or antiferroelectric ordering, and discuss its relevance to material design.

Results

Phase Diagram. We show the $T - \eta$ phase diagram of our model in Fig. 1*B*, where η represents the degree of shape anisotropy and $\eta = 0$ corresponds to the spherical dipoles (43) (*Materials and Methods* and *SI Appendix, A*). We fix the pressure at a high value so that the crystalline state is stable for a broad temperature range. For η close to zero, there are three stable phases: the equilibrium liquid, paraelectric crystal (plastic crystal characterized by long-range translational order but without orientational order), and ferroelectric crystal (Fig. 1*C*), from high to low temperature. Here the paraelectric–ferroelectric phase transition is of second order (*SI Appendix, B*). The crystalline structure of the paraelectric phase is either face-centered cubic ($Fm\bar{3}m$) or hexagonal closed packed ($P6_3/mmc$) with almost equal probability; upon transition to the ferroelectric phase, it transforms into a rhombohedral ($R\bar{3}m$) or hexagonal ($P6_3mc$) structure by dipole alignment accompanying the associated change of (111) interlayer spacing. With increasing η , the paraelectric–ferroelectric transition temperature decreases since the ferroelectric attractive interaction decreases (Fig. 1*A*). Eventually, an antiferroelectric phase with a monoclinic ($P2_1/m$) structure (Fig. 1*D*) is formed from the ferroelectric phase via a strongly first-order transition (see *SI Appendix, C* for the details of the crystalline structure). At $\eta = 1.4$, the ferroelectric–antiferroelectric phase transition temperature coincides with that of the paraelectric–ferroelectric phase transition, indicating the presence of a triple point. Interestingly, a strong electrostrictive coupling for larger η changes the nature of the (metastable) paraelectric–ferroelectric transformation from second order to

Fig. 1. Phase behavior. (A) Schematic representation of electro-mechanical coupling in our model. Since the dipolar interaction changes its sign depending on the particle arrangement, the ferroelectric/antiferroelectric ordering crucially depends on the aspect ratio of the spheroids and the applied strain. (B) Equilibrium (η, T) -phase diagram of our model (see *Materials and Methods* for the calculations). The solid and dashed lines are the phase boundaries between equilibrium phases and those between metastable states, respectively. The phase transitions are first order for the antiferroelectric–ferroelectric/paraelectric transitions (black line) and the crystal–liquid phase transition (blue line). The transition between the stable ferroelectric and the paraelectric phase for $\eta < 1.4$ (solid red line) is second order, whereas the one between their metastable phases for $\eta \geq 1.4$ (dashed red line) is weakly first order due to the electrostrictive coupling between polarization and strain (*SI Appendix, B*). (C) A ferroelectric phase observed for $\eta = 1.0$ and $T = 0.6$. The color denotes the molecular orientation; we can see that almost all of the particles align along the same direction. (D) An antiferroelectric phase observed for $\eta = 1.6$ and $T = 0.6$. Two kinds of ferroelectric planes (distinguished by color) are stacked alternately, leading to cancellation of macroscopic polarization. The snapshots in C and D are obtained from the low- T part on cooling from the simulations displayed in Fig. 2*A* and *B*, respectively. In C and D, color fluctuation reflects orientation fluctuation, which is stronger in the ferroelectric state (C) than in the antiferroelectric one (D) (Fig. 3). We note that time-averaged orientation reduces fluctuation and coincides with that expected for the assigned space groups in the main text. (E) Color legends of the dipole orientation.

ing and heating paths, indicating the second-order nature of this phase transition. We note that the local nematic order $\langle Q \rangle$, the average of the magnitude of local nematic order (see [SI Appendix, E](#) for the detailed definition), also develops upon cooling, since the dipole moment is set along the shape anisotropy (or long) axis of each particle.

On the other hand, the paraelectric–antiferroelectric transition at large η is accompanied by a large temperature hysteresis, as shown in Fig. 2B. We can see that the dipolar order $\langle P \rangle$ abruptly decreases and almost vanishes upon cooling (Fig. 2B, red curve), whereas the nematic order increases discontinuously to have a large value even when the polarization vanishes (Fig. 2B, blue curve). This is a clear signature of the emergence of antiferroelectric long-range order below $T \cong 0.66$. The macroscopic polarization should be zero for both paraelectric and antiferroelectric phases. However, since we define $\langle P \rangle$ as the average of the magnitude of local polarization, it need not be zero and reflects the degree of local polarization fluctuation. Thus, the abrupt change in $\langle P \rangle$ upon phase transition is correlated with the change in the dielectric constant (Fig. 2C). The phase transition shows a large hysteresis on cycling the temperature, indicating the strong first-order nature of the antiferroelectric phase transition. We also show the temperature dependence of the dielectric constant for $\eta = 1.0$ and 1.6 (SI Appendix, F). The paraelectric–ferroelectric transition at small η is accompanied by a much larger change in the dielectric constant than the paraelectric–antiferroelectric one at large η (Fig. 2C). This is primarily because smaller anisotropy allows larger orientational fluctuations of dipoles due to less steric hindrance. Furthermore, dipole fluctuations are larger in the ferroelectric phase than in the antiferroelectric one even for the same η , which is discussed later (Fig. 3). The transformation of the crystal structure can also be clearly seen in Fig. 2D, where we show the change of a special structural order parameter that has a nonzero value only in the antiferroelectric phase (SI Appendix, E). To further confirm that this ordered state really has antiferroelectric order, we also examine the dielectric response to an external electric field. As shown in Fig. 2E, we observe a double hysteresis response (red curve) to the applied electric field, a characteristic of the antiferroelectric phase. Since the dipole moment is set along the long axis of the spheroid particle in our model, the polarization response is automatically accompanied by a large strain response, as shown by the blue curve in Fig. 2E. We note that this response is electrostrictive, and not piezoelectric, since the space group of the antiferroelectric phase is centrosymmetric $P2_1/m$.

The large hysteresis loops in Fig. 2 *B* and *E* imply a large free-energy barrier for the phase transformation. This indicates that there should be a long incubation time for spontaneous nucleation of antiferroelectric domains in the ferroelectric phase (see *SI Appendix, H* for the dynamical process of nucleation). Indeed, this is confirmed by the frequency dependence of the polarization response (Fig. 2*F*): With increasing the frequency, the double-hysteretic response characteristic of the antiferroelectric phase disappears. This frequency dependence indicates that there is not enough time for the system to transform back to the antiferroelectric state under such a high-frequency modulation. This can be confirmed by the fact that the relaxation time ($\simeq 100t_0$) (*SI Appendix, K* and Fig. S8) is longer than the time period of field switching at the highest frequency. This highlights the interesting possibility of controlling both the strain and the polarization responses to an external electric field by tuning the degree of particle anisotropy (η in our model). Indeed, the field required to induce a ferroelectric state from an antiferroelectric one crucially depends on η . The hysteresis loop becomes smaller for η close to the phase boundary, as shown in Fig. 1*B*.

The Origin of Slow Dynamics of the Ferro-to-Antiferro Transformation. Now we consider why the response is so slow. According to

Next we show how ferroelectric order and antiferroelectric order respond to the change in temperature (*SI Appendix, D*). The results of the paraelectric–ferroelectric transition at small η are shown in Fig. 24. The dipolar order $\langle P \rangle$, the average of the magnitude of local dipolar order (see *SI Appendix, E* for the detailed definition), grows steeply around $T = 0.75\epsilon/k_B$ upon cooling. We can see almost the same polarization behavior for both cool-

Fig. 3. Rotational dynamical structure factor $S_R(q, \omega)$ of ferroelectric and antiferroelectric phases, showing the difference in vibrational dynamics between ferroelectric and antiferroelectric states. See [SI Appendix, J](#) for the definition of $S_R(q, \omega)$ and the calculation of vibrational density of states.

classical nucleation theory, this timescale is determined by the free-energy barrier to overcome and the dynamics of elementary excitation. The free-energy gain comes from the formation of the more stable phase, whereas the penalty comes from the formation of the domain interface. In our system, the nucleation should be accompanied by cooperative displacement and reorientation of the particles in the same hexagonal plane over the size of a critical nucleus. This is because such cooperativity is necessary to avoid charging (represented by $\nabla \cdot \mathbf{P}$, where $\mathbf{P}$ stands for polarization field) at the interface, since it costs large electrostatic energy (*SI Appendix, H*). Note that flipping of a dipole in a ferroelectric state inevitably results in charging at both ends at the dipole, but not in perpendicular directions. This requires cooperativity in dipole rotation along the direction of the long axis of spheroids. The probability to have such cooperative reorientation may steeply decrease with domain size, simply because the number of particles involved increases. This extra physical constraint arising from the avoidance of charging, which is a universal electrostatic factor governing the kinetics of the polarization ordering, explains why the ferroelectric-to-antiferroelectric transition exhibits a large hysteresis and requires a long incubation time.

Furthermore, the dipolar interaction also affects another important factor governing the slow dynamics: It is the distance between adjacent spheroids, which controls steric hindrance to rotational motion. This structural factor is responsible for the asymmetry in the response between ferro-to-antiferro and antiferro-to-ferro transformations. To see this, we calculate the vibrational entropy difference in these phases, which stems from the difference in the degree of steric hindrance to particle rotation. As can be seen in Fig. 14, spheroids have more space to fluctuate for the ferroelectric arrangement than for the antiferroelectric one: The nested structure of the latter tends to inhibit rotational fluctuations. Indeed the average angular amplitude of rotational vibration of the dipoles relative to their average orientations becomes 23° for the ferroelectric state and 16° for the antiferroelectric state, although these fluctuations are isotropic for both states. The antiparallel dipole arrangement in the antiferroelectric phase causes both electrostatic and steric constraints on the particle motion: The strong electrostatic attraction between adjacent antiparallel spheroids causes a strong constraint on the relative motion of spheroids. Furthermore, the distance between the nearest antiparallel neighbors becomes shorter by approximately 5% upon phase transformation from the ferroelectric to the antiferroelectric state by the attractive interaction (*SI Appendix, I and Fig. S6*), causing a strong geometrical constraint on rotational motions. These electrostatic and geometrical constraints result in suppres-

sion of the rotational motion in the antiferroelectric phase. As we can see in Fig. 3, the ferroelectric phase has more low-energy (or softer) excitation modes of rotational nature compared with the antiferroelectric phase. The presence of the distinct gap in the excitation frequency for the antiferroelectric phase indicates not only the absence of low-frequency coherent rotational modes but also the presence of a resonance frequency, the latter of which is reminiscent of the magnon dispersion relation in ferromagnetic and antiferromagnetic materials with uniaxial anisotropy (50). We note that in our system the uniaxial anisotropy stems from the steric hindrance to the dipole moment. This implies that the resonance frequency can be controlled by varying the shape anisotropy of the spheroids. We note that we confirm that there is little difference in the translational vibrational modes and configurational entropy between the two phases (*SI Appendix, J and Fig. S7*).

Here we note that the entropy difference between ferroelectric and antiferroelectric phases implies an inverse electro-caloric effect (*SI Appendix, K* and Fig. S8), which has been observed in some antiferroelectric inorganic oxides (19, 51).

Mechanical Control of Antiferroelectric Phase. Finally we show interesting electro-mechanical coupling observed under external stress, indicating the possibility of mechanical manipulation of the antiferroelectric phase. Larger particle anisotropy η means a stronger coupling between anisotropic mechanical stress and particle alignment. Thus, an externally applied anisotropic stress may affect the phase behavior via electro-mechanical coupling. In Fig. 4, we show examples of such a polarization response to a uniaxial stress. Depending on the direction of the applied stress and temperature, the initial

Fig. 4. Mechanical switching of antiferroelectric order. By applying a uniaxial compression to an antiferroelectric state, we can induce an antiferroelectric to antiferroelectric (AF to AF) polarization reorientation. By applying a uniaxial stretching and compression to the same initial state in appropriate directions, on the other hand, we can induce antiferroelectric to ferroelectric (AF to F) and antiferroelectric to paraelectric (AF to P) phase transitions, respectively, which are accompanied by large changes in the dielectric permittivity. See [SI Appendix, L](#) for the details of the calculations and the kinetics of the phase changes.

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