# Electrically variable interfaces in polymer nanocomposite dielectrics

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Polymer nanocomposites generally exhibit unexpected dielectric/electrical performance far beyond the sum of every component, which is mainly due to the interface effect induced by the differences in structures and properties between the nanofillers and the polymer matrix. However, understanding the capricious interface effect in different polymer nanocomposites remains a major challenge. Here, we perform density functional theory calculations to investigate the atomic/molecular configurations and local charge behaviors of heterogeneous interfaces between the fillers of perovskites, oxides, two-dimensional materials, and polar/nonpolar polymers. Our findings demonstrate that atomic reconfiguration takes place during the formation of the inorganic/organic interface in order to minimize the overall energy of the system. Significant charge accumulation occurs at heterogeneous interfaces due to electron redistribution, especially for the examples of HfO<sub>2</sub> and negatively charged Ca<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>. When applying an electric field, local polarization, especially around the interface, will be distorted and enhanced as a result of interfacial interaction. Even for the nonpolar polymer with linear dielectric oxides such as TiO<sub>2</sub>, induced dipole moments also appear near the interface, leading to the improvement of overall polarizability. The outcomes of our study verify that the variable electrical behaviors at the interfaces are highly dependent on the feature of every component constituting the inorganic/organic interface, which offers valuable insights for optimizing the experimental design of heterogeneous interfaces in polymer nanocomposites.

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# I. INTRODUCTION

Dielectric capacitors, characterized by electric dipoles to control charge, have been extensively utilized in portable electronics, pulse power systems, and electric vehicles due to their ultrahigh power density, and high working voltage [1]. However, the use of traditional single-phase dielectrics comes with inherent limitations, such as the low breakdown strength  $E_{\rm b}$ , poor flexibility of ceramic dielectrics and the low permittivity  $\kappa$  of polymer dielectrics, resulting in relatively low energy density  $U_{\rm e}$ . Hence, it is increasingly difficult for single-phase dielectrics to meet the requirements of high energy storage performance with the inevitable development trend of integration and versatility. To deal with the above challenges, polymer nanocomposites (PNs) have been proposed by incorporating high- $\kappa$  ceramic fillers into the high- $E_b$  polymer matrix [2]. The hope is that PNs can combine the advantages of two single-phase components to achieve both high- $\kappa$  and high- $E_{\rm b}$ , thereby exhibiting high  $U_{\rm e}$  [3]. Although a great deal of effort has been put into exploring high-performance PNs, most of the experimental explorations have a large gap with the expected performance. The primary reason behind the problem lies in the complex nature of the interfaces between the inorganic fillers and the organic matrix. Especially when the filler sizes approach nanometric dimensions, the surface of the fillers and the interface/interphase with the surrounding polymer occupy a considerable proportion of the overall volume of PNs, as much as 50–70% [4], as detailed in Fig. 1(a). Therefore, the interfacial behaviors, which differ dramatically from each single-phase component, play an indispensable role in determining the overall energy storage performance of PNs [5]. However, the interface characteristics in different PNs and their effects on energy storage performance have not been fully elucidated.

The interface region within PNs, which is sometimes regarded as the third phase, ordinarily initiates from the surface of nanofillers, traverses the modified layer and the diffuse layer and ultimately extends to the matrix region [6]. Electrical or dielectric continuity in PNs will be broken or altered at the interface due to the large property mismatch and complex configuration variations, as illustrated in Fig. 1(b). For example, previous studies [7–9] have shown that the large interface area in PNs would enhance the exchange coupling effect via the dipole interface layer, leading to an elevated polarization level, dielectric response, and breakdown strength. In addition, the interface can induce changes in the molecular structure of the polymer, such as free volume, crystallinity,

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FIG. 1. The schematic diagram of PNs with (a) a multitude of heterogeneous interfaces, where significant charge redistribution occurs. (b) Some changes in material properties at the interface, such as electrostatic potential distribution and dielectric constant modulation. The interface thickness d is usually on nanometric scale. (c) The representative inorganic fillers with three primary categories: namely perovskites, oxides, and two-dimensional layered structures. (d) The polymer structures of the nonpolar iPP and polar PVDF used as the matrices in this work.

and polymer chain configuration, thereby influencing the dielectric properties of the polymer [10,11]. However, the discontinuity between the inorganic nanofillers and the polymer matrix leads to the induction of various defects, resulting in significant local field fluctuations at the interface [12]. For instance, the high polarization of ferroelectric nanoparticles leads to a significant concentration of counter charges within the polymer. The transverse movement of charges in the interface region further amplifies this concentration, resulting in a notable increase in interfacial electric field and subsequent enhancement of both polarization [13]. Localized enhancement of the interfacial electric field can also create weak points that reduce the breakdown strength of the PNs. At the same time, electron and atom reconfiguration will occur at the interface under the interfacial electric field [14,15]. Extensive reconstruction of the Fermi surface and ion relaxation processes, such as charge transferring, are involved in electron reconstruction, while atom reconstruction involves stoichiometric changes such as the formation of point defects. All the factors mentioned above may individually or collectively impact the energy storage performance of PNs, which also makes the interface effect a tricky challenge that has always been difficult to figure out.

All along, understanding the interface characteristics has been a key pursuit in the field of energy storage PNs. In terms of theoretical models, various theories have been proposed to describe the electrical and dielectric behavior at the interfaces in PNs, such as the classical double-layer model [16] and the multicore model [17]. Guided by the above models, a multitude of studies on improving the dielectric properties of PNs have been carried out from different lengths and time scales, such as the design of different shapes and surface modification of nanofillers, etc. [18]. The existing theoretical models, however, lack quantitative description of the interface structure and properties, thereby hindering the direct establishment of a correlation between interface properties and macroscopic dielectric properties. For the experimental exploration, with the advancement of technology and the endless emergence of characterization methods, three primary characterization strategies have been employed to study and comprehend the matrix/filler interfaces: (i) bulk-based nanocomposite measurements, such as Fourier transform infrared spectroscopy [19]; (ii) scanning probe microscope-based measurements, such as in situ measurements of interface regions by Scanning Probe Microscopy (SPM) [20]; (iii) model-based measurements, such as the utilization of ultrathin model samples to detect the confinement characteristics of the interface via surface-sensitive techniques [21]. These methods can extract interface properties, such as interface chemical structure and composition, polarization, and relaxation phenomena. However, these characterization strategies necessitate exacting requirements on sample quality and spatial resolution, as well as many challenges to be overcome, including interference noise, difficulty in controlling the interface condition, and the lack of theory to analyze the interface signal from the overall signal [22]. Therefore, analyzing the contribution of

interface to overall performance by experiment remains a persistent challenge. It is crucial to emphasize that studying the interfaces in PNs aims to advance scientific understanding of this pivotal issue, eventually expediting more new materials design and applications.

In this study, we investigate the inorganic/organic interfacial properties in various nanocomposites at atomic and molecular levels using density functional theory (DFT). Three fundamental categories of inorganic nanofillers are considered in this work as displayed in Fig. 1(c), namely high- $\kappa$  ferroelectric perovskites [including BiFeO<sub>3</sub>(BFO), BaTiO<sub>3</sub>(BTO), PbTiO<sub>3</sub>(PTO), SrTiO<sub>3</sub>(STO), BiNaTiO<sub>3</sub>(BNT)], linear oxides (including Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, MgO, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>), and two-dimensional (2D) layered materials [(including h-BN, Ca<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>(CNO), montmorillonite)]. For the polymer matrix, we examine two distinct cases to construct different heterogeneous interfaces: a polar Polyvinylidene Fluoride (PVDF) polymer and a nonpolar isotactic polypropylene (iPP) polymer, as displayed in Fig. 1(d). We investigate the behavior of atomic reconfiguration and charge transfer at a variety of heterogeneous interfaces. Furthermore, we employ electric field-induced polarization measurements to elucidate the atomic-level alterations in local dielectric properties induced by surfaces and interfaces.

# **II. CALCULATION METHODS**

All DFT calculations in this work were performed using the Vienna ab initio simulation package (VASP) [23]. Considering the size and computational efficiency of the interface model, we adopt the ideal crystal structure and Cartesian coordinates. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof [24,25] and the projector augmented wave [26] were used to describe the exchange-correlation functional and nucleus-electron interactions, respectively. In addition, due to the van der Waals interlayer interaction at the inorganic/organic interface, it is necessary to use the Becke-Johnson damping method [27] to correct it. The cut-off energy was set to 450 eV and the k-point meshes of the Brillouin zone was chosen to be  $6 \times 6 \times 1$ . The atomic positions were relaxed until the force convergence standard was less than 0.05 eV/Å and the total energy convergence reached  $10^{-7}$  eV. The slab structures utilized for investigating the inorganic/organic polymer interfaces are constructed in orthogonal supercells under periodic boundary conditions, with periodically repeated slabs separated by a vacuum of approximately 10 Å along the z axis. The dipole correction technique is introduced to ensure the compatibility of the field across the simulation cells [28]. All the structure and volumetric data in this study were visualized using the VESTA code [29].

The initial perfect crystals were obtained from the Material Project database [30], and we subsequently conducted structural relaxation on them. The lattice constants after relaxation and space groups are shown in Table S1 in the Supplemental Material [36], and the agreement with the experimental results is within 4% by standard DFT calculations. If the DFT+U method is employed, it may enable more precise calculated results of electronic structure of strong correlation materials [28]. It should be noted that this study aims

to be a qualitative study that highlights the differences in electronic properties among stacked interfaces under the same approach.

The energy of forming an interface between two materials (formation energy) is defined as the energy difference between the interface system and the constituent slabs in their lowest energy bulk phase, divided by the interface area,

$$E_{\text{formation}} = \frac{E_{\text{interface}} - (E_{\text{slab, inorganic}} + E_{\text{slab, organic}})}{S}, \quad (1)$$

where  $E_{\text{interface}}$  is the energy of the interface structure, and  $E_{\text{slab}, A}$  is the energy associated with a slab of material A. This allows us to ignore the energy cost of cleaving the two slabs and focus solely on the energy required for combining them into an interface. The utilization of formation energy enables the assessment of structural stability across various interfaces, with lower formation energies indicating more favorable energetic conditions.

When constructing the interface structure, we varied the separation, defined as the interface width between two surfaces, ranging from 1.0 to 6.0 Å and calculated the total energy of the interface under each separation. When the interface width falls below 1.0 Å, a significant repulsion energy is generated. Whereas, as the separation exceeds 6 Å, the system energy gradually converges to the sum of energies from both components in their completely separated states. Therefore, we calculated the interfacial energy according to the separation of this range and fit the universal binding energy relation (UBER) [31], which can be expressed as

$$W_{\rm ad}(d) = -W_0 \left[ 1 + \frac{d - d_0}{l} \right] \exp\left(-\frac{d - d_0}{l}\right),$$
 (2)

where  $W_{ad}(d)$  is the relative energy of the interface system with the separation d, and l is mainly used as parameters related to the interface. The relative energy  $W_{ad}(d)$  is defined as  $W_{ad}(d) = [E_{int}(d) - E_{int}(\infty)]/S$ , with respect to the state of infinitely separated surfaces, where  $E_{int}(d)$  is the total energy of an interface with a separation d.  $W_{ad}(d)$  reaches its minimum value of  $W_0$  at the equilibrium width  $d_0$  [32].

#### **III. RESULTS AND DISCUSSIONS**

## A. Structure and stability

For the polar polymer, we choose the  $\beta$ -phase crystal of PVDF due to its perpendicular dipole moment with respect to the chain axis orientation, resulting in its large polarity and high relative dielectric constant [33]. This polar orientation gives rise to two available types of slabs: H-terminated (PVDF-H) and F-terminated (PVDF-F), as depicted in Fig. 1(d). While for nonpolar iPP, we only consider the most common crystal phase, namely the  $\alpha$  phase [34]. Although its unit cell is monoclinic, an orthorhombic supercell is employed instead of the monoclinic one for modeling and complexity reasons. Here, the iPP slab comprised of double-methyl termination and a bilayer parallel to the ac plane is utilized to construct the interface, with both chain conformation and length remaining unchanged [see Fig. 1(d)]. When composing the interfaces, the lattice mismatch of the two polymers along chain direction is controllable, ensuring a stable chain configuration. For nanofillers oriented along



FIG. 2. The atomic structure model of  $BaTiO_3/PVDF$  and  $BaTiO_3/iPP$  in the view of [001] plane in the unrelaxed state. The  $TiO_2$ -terminated with (a) H- and (c) F-, and BaO-terminated with (b) H- and (d) F-. The (e)  $TiO_2$ -terminated and (f) BaO-terminated of  $BaTiO_3/iPP$  interfaces. (g) The interfaces' relative energies versus interface width. The markers are calculated values, and the curves are fitted UBER models. (h) The separations of all stable interface models in this work.

different crystal planes, surface atoms may possess defects or active sites. These sites can participate in chemical reactions or adsorption processes, thereby influencing overall performance. Taking BTO as an example, the most stable orientation is along the (001) direction, and there are two  $2 \times 2$  slabs can be adopted: BaO-terminated and TiO<sub>2</sub>-terminated, as is shown in Figs. 2(a)–2(f). According to Harrison's bond-counting rules [35], both surfaces should be charge neutral.

To find the stable configurations of diverse interfaces, we calculate the formation energy with different terminations and separations. For the example of BTO/PVDF interface, the equilibrium interfacial separation is 2.783 and 3.036 Å for the configurations depicted in Figs. 2(a) and 2(b), respectively, while the corresponding formation energies are -0.31278 $eV/Å^2$  and  $-0.31022 eV/Å^2$ . The TiO<sub>2</sub>-terminal /PVDF-H configuration is identified as the most stable interface after comparing with other interface configurations. Similarly, in the iPP matrix, the formation energy composed of TiO<sub>2</sub>terminated is found to be the lowest at  $-0.01114 \text{ eV/}\text{Å}^2$ , with a corresponding equilibrium separation of 2.233 Å. The system energy obtained based on UBER varies with interface separation, as illustrated in Fig. 2(g). For all inorganic/organic interfaces in this work, we follow the above approach to determine the interface models and the calculated interfacial separations are shown in Fig. 2(h). All of these values are around  $1 \sim 3$ Å, indicating that the composite interfaces are formed by van der Waals interactions.

The optimized stable configurations of BTO/PVDF and BTO/iPP are displayed in Fig. S1 in the Supplemental Material [36] in the view of the (001) and (010) planes, while the relaxed structures of all other interface models can be observed in Fig. S2 [36]. As can be seen, on the left side of the interface, the perovskites  $ABO_3$  fillers with BO<sub>2</sub>-termination exhibit an incomplete lattice at its surface, which can lead

to surface roughness and defects. These defects induce lattice reconfiguration and atomic rearrangement to fill or adjust the gaps and irregularities on the surface [37]. The main features are the apparent distortion of the Ti-O octahedron and the deviation of the Ti ions from the center of their respective octahedron, thereby perturbing the original periodic potential field of the lattice. The degree of deviation gradually decreases as it extends into the bulk. For instance, in the BTO/PVDF system, the bond length of Ti-O near the interface is 2.0069 Å, which is higher than 1.9975 Å of Ti-O within bulk (see Fig. S1(a) [36]). The Ti at the surface is approximately 0.137 Å away from the center of the Ti-O octahedron, whereas internally situated Ti exhibits a deviation of about 0.03 Å. While for the BTO/iPP system in Fig. S1(b) [36], the Ti-O bond length and deviation of Ti ions near the interface are 2.2038 and 0.153 Å, respectively, surpassing those of the BTO/PVDF system. This trend is consistently demonstrated across various interface configurations. The low interface interaction between the nonpolar polymer iPP and the filler is responsible for this phenomenon, resulting in increased active space of the nanofillers and a consequent reduction in surface energy, as illustrated in Fig. S3(a) [36]. In the case of oxides, the chemical environment of the surface oxygen atoms may significantly differ from their internal crystal structure. This disparity results in variations in oxidation states, oxygen suspension bonds, or oxygen vacancies for oxygen atoms on the surface, particularly in SiO<sub>2</sub> and TiO<sub>2</sub>, as can be seen in Fig. S2 [36]. Consequently, a greater extent of atomic reconfiguration is required to minimize the surface energy and enhance crystal stability.

For the polymer chains situated on the right side of the stable configuration in Fig. S2 [36], a majority of polymer chains exhibit remarkable resilience in maintaining their initial chain orientation. This phenomenon can be primarily attributed to the confinement effect exerted by nanofillers



FIG. 3. The electron transfer isosurfaces and charge displacement curve (CDC) along z of (a) perovskite fillers, (b) oxides fillers, (c) 2D layered fillers with PVDF matrix. The schematic diagrams above the curve represent BFO/PVDF,  $HfO_2/PVDF$ , and CNO/PVDF, respectively. The yellow and blue isosurfaces represent charge accumulation and depletion. The gray area denotes the interface region.

[38], which restricts their migration and promotes orderly arrangement through enhanced van der Waals adsorption at the interface. Figure S3(b) [36] demonstrates that the presence of nanofillers results in a decrease in polymer chain energy, suggesting their potential for augmenting the crystallinity [39]. While in certain oxide systems, more pronounced distortion of the chains becomes evident. On one hand, some oxides and polymers may exhibit large lattice mismatches, such as about 17.7% for Al<sub>2</sub>O<sub>3</sub>/iPP system, resulting in the elongation of polymer chains. On the other hand, the robust chemical properties of the surface oxygen atoms enhance the interaction at the organic/inorganic interface such as TiO<sub>2</sub>/PVDF, thereby inducing polymer chain torsion or reorganization to accommodate stress variations.

#### **B.** Electronic properties

We then investigate the electronic properties of these stable interface configurations, quantitatively characterizing the electron behaviors by analyzing the interfacial charge transfer. The charge displacement curve (CDC) is given as

$$\Delta Q = \int_{-\infty}^{z} \Delta q dz = \int_{-\infty}^{z} \left[ \iint (\rho_{\text{interface}} - \rho_{\text{slab, inorganic}} - \rho_{\text{slab, organic}}) dx dy \right] dz, \quad (3)$$

where  $\rho_{\text{interface}}$  and  $\rho_{\text{slab, A}}$  represent the charge density of heterostructure and their isolated systems, respectively. The calculation results of PVDF-based interfaces and iPP-based interfaces are shown in Figs. 3 and 4 (the plane-average charge difference  $\Delta q$  is shown in Fig. S4 [36]), respectively. The positive and negative gradients of  $\Delta Q$  indicate electron accumulation and depletion. Overall, the electron redistribution within the contact interface region is evidently significant, and it accumulates to the maximum value at the interface followed by a gradual decay towards the bulk. The crucial point lies in the fact that the variation of polymer polarity solely affects the magnitude of the relative value of charge transfer, while leaving their trend unaffected.

For polar PVDF-based systems (see Fig. 3), the charge transfer among different fillers at the interface is significantly distinct. For the filler of perovskite ABO<sub>3</sub>, the electron accumulation at the interface exhibits a similar pattern of peak distribution, but different peak values. For example, BFO/PVDF system exhibits the highest charge exchange with a highest value of 0.188 e, followed closely by the BTO/PVDF system with that of 0.137 e. This phenomenon can be attributed to the similarity in their incomplete lattices, and the isosurfaces of charge transfer illustrated in Fig. 3(a) also provides evidence that the primary contribution originates from the Ti and O atoms. The Bader charge analysis reveals a significant distinction in terms of the A-site atoms (Figs. S5(a) and S5(b) [36]). For example, the Ti atoms exhibit a comparable electron loss, while the surface Ba atom loses 2.00 e, Pb loses 1.71 e, and Sr loses 1.64 e, which is consistent with  $\Delta Q$ . This is in line with the findings of Zhong *et al.* [40], who demonstrated that the electron migration and surface or interface properties of transition-metal-oxides strongly depend on specific surface terminations, reconstruction, and other microscopic surface details. While for simple oxide systems [Fig. 3(b)], some oxides demonstrate superior charge transport properties, such as HfO<sub>2</sub>/PVDF system showing a charge transfer of 0.493 e, whereas fillers like MgO or Al<sub>2</sub>O<sub>3</sub> exhibit lower electron exchange. In comparison to ABO<sub>3</sub> fillers, simple oxides tend to possess more surface defects, such as oxygen vacancies, that can serve as electron donors, thereby reducing the recombination of hole-electron pairs and consequently facilitating efficient charge transfer [41]. Bader charge analysis (Figs. S6(a) and S6(b) [36]) demonstrates a variety of oxidation states on the oxide surfaces. For instance, the oxygen atom adjacent to the interface in the HfO<sub>2</sub>/PVDF system exhibits a significantly reduced charge of 0.493 e compared to its value within the bulk. In the case of 2D layered materials



FIG. 4. The electron transfer isosurfaces and charge displacement curve (CDC) along z of (a) perovskite fillers, (b) oxides fillers, (c) 2D layered fillers with iPP matrix. The schematic diagrams above the curve represent BTO/iPP, HfO<sub>2</sub>/iPP, and CNO/iPP, respectively. The yellow and blue isosurfaces represent charge accumulation and depletion. The gray area denotes the interface region.

[Fig. 3(c)], the CNO/polymer system exhibits a substantial magnitude of charge transfer, reaching 0.454 e, whereas other systems show minimal charge transfer. This phenomenon can be attributed to the negatively charged surface properties of CNO, thereby facilitating a significant charge transfer as an electron donor. Conversely, the symmetrical structure and high barrier height (see Figs. S7(c) and S7(f) [36]) of other 2D materials impose limitations on electron migration when interacting with polymers.

Compared to polar PVDF, the molecular chain of nonpolar iPP primarily consists of carbon and hydrogen, resulting in a relatively simplistic chain structure that diminishes its interaction with the fillers. The charge transfer diagram in Fig. 4 reveals that the charge exchange of the iPP/perovskite system is minimal, with the BTO/iPP heterostructure measuring only 0.035 e, which is four times smaller than that observed in the PVDF/perovskite system. The charge density diagram depicted in Fig. 4(a) indicates that charge transfer occurs within a limited region of the interface. While the charge transfer of the oxide fillers in the iPP matrix is comparable to that in the PVDF matrix [see Fig. 4(b)], with TiO<sub>2</sub> transferring 0.25 e to iPP and 0.33 e to PVDF polymer. This suggests that the surface properties or crystal structure of the oxide itself may be the primary determinant of charge transfer. Such consistency expands the range of applications and possibilities of oxides in various systems. It is noteworthy that the charge transfer of CNO in the iPP matrix exhibits a remarkably high level, and the interfacial charge transfer of the CNO/iPP system reaches 0.38 e, as shown in Fig. 4(c). This discovery underscores the inherent properties and potential advantages possessed by CNO nanosheets in enhancing dielectric and energy storage performance. Overall, the  $\Delta Q$  of the PVDF matrix exceeds that of the iPP matrix, indicating a higher efficiency in driving electron flow by the polar PVDF. In this scenario, the loss near interface C for the PVDF matrix is 0.95 e, while H and F exhibit gains of 0.50 e and 0.270 e, respectively. Similarly, in iPP, C loses 0.947 e and H gains 0.515 e. The findings indicate

that the presence of polar atoms in the polymer chains leads to an asymmetric charge distribution, resulting in an electric field that facilitates charge exchange in the surrounding environment [42].

Finally, we elucidate the charge transfer mechanism by analyzing the planar average electrostatic potential in Fig. S7 [36]. The polymer exhibits a higher electrostatic potential compared to that of nanofillers, resulting in the establishment of a built-in electric field  $(E_{in})$  which gradually aligns their respective Fermi energies. The result is an upward bending of the conduction band and valence band of the polymer, accompanied by a downward bending of the nanofillers' energy levels [43]. Charge exchange takes place within the interface region until Ein is fully compensated. Compared with the PVDF system, the  $E_{in}$  formed in the iPP/nanofillers systems is smaller with lower charge transfer. The charge transfer behavior can also be reflected by the valence band offset across the interface [44], which represents the energy barrier that must be surmounted for electron transfer to occur. The predominant occurrence of charge exchange takes place at the interface and surface, thus making it contingent upon the material's surface properties as well. Large space charge transfer at the interface between organic and inorganic can enhance the binding force, facilitate effective coupling, and improve the strength and stability of the interface [45]. However, excessive charge transfer may also result in significant dielectric loss. It is essential to consider multiple aspects of material properties and strike a suitable balance between charge transfer and dielectric characteristics for optimal utilization in dielectric applications.

#### C. Induced electric polarization

Quantitative comprehension of atomic-scale electrical response across layered heterostructures can provide a basis for understanding the factors that control the properties of interfaces between dielectric fillers and matrices. We then study the local microscopic polarization under an electric field, which



FIG. 5. Microscopic polarization along the z axis in PVDF matrix with (a) perovskite fillers, (b) oxide fillers, and (c) 2D layered fillers, averaged along the x-y plane. (d) The polarization charge distribution of BFO/PVDF,  $TiO_2/PVDF$ , CNO/PVDF, where the yellow and bule isosurfaces represent the induced positive and negative charge. Microscopic polarization occurs from areas of positive charge towards regions of negative charge.

pertains to the emergence of an electric dipole moment within a material at the microscopic scale due to the arrangement or orientation of its constituent dipoles. In this study, we incorporate the theory of position-dependent-only dielectric constants [46,47] to access various interfacial systems. The local microscopic dielectric polarization  $\bar{p}(\mathbf{r})$  can be obtained from the field-induced charge density  $\rho_{ind}(\mathbf{r})$  through the inmedium Maxwell equation [48],

$$\nabla \cdot \mathbf{p}(\mathbf{r}) = -\rho_{\text{ind}}(\mathbf{r}). \tag{4}$$

For our slab oriented along the x-y plane, Eq. (4) can be simplified as

$$\frac{d}{dz}\bar{p}(z) = -\bar{\rho}_{\rm ind}(z),\tag{5}$$

where  $\bar{p}(z)$  and  $\bar{\rho}_{ind}(z)$  are the polarization and induced charge density integrated over the *x*-*y* plane, respectively. The  $\bar{\rho}_{ind}(z)$ can be evaluated as  $\bar{\rho}_{ind}(z) = \bar{\rho}_{ind}(+\delta) - \bar{\rho}_{ind}(-\delta)$ , representing the difference of the charge density between positive and negative electric field. Equation (5) can be solved as follows:

$$\bar{p}(z) = \bar{p}_{-\infty} - \int_{-\infty}^{z} \bar{\rho}_{\rm ind}(z') dz'.$$
(6)

In order to apply a finite electric field  $E_z^{app}$  parallel to the *z* direction, an artificially generated planar dipole layer is introduced in the middle of the vacuum by dipole correction technique [49]. This dipole layer corrects the discontinuity of the electrostatic potential at the boundary of the supercell, thus realizing the controllable application of limited electric field. The polarization changes of slabs under  $E_z^{app}$  without lattice relaxation were then investigated. Figure S8 [36] illustrates the structure and local polarization of the single-phase dielectrics, revealing a smooth attenuation of polarization from surface to vacuum with oscillations between chains. This implies that a lower polymer chain density may lead to reduced polarization and effective dielectric constant as would be expected [50]. The same oscillation occurs in the single-phase BTO plate, accompanied by polarization peaks resulting from the asymmetrical arrangement of atoms on both surfaces. In this work, a value of 0.2 V/Å was chosen to study the local polarization response.

The position-dependent-only polarization curves of all heterogeneous systems based on PVDF are shown in Fig. 5, where the left side of the gray area corresponds to PVDF. It is worth noting that all polarization responses are changed after the organic and inorganic interfaces were formed. Among perovskite fillers, the BFO/PVDF system exhibits the highest local polarization enhancement, as is illustrated in Fig. 5(a). For the PVDF on the right side of the interface, compared to the single-phase PVDF with a maximum local polarization of 7.73  $\mu$ C/cm<sup>2</sup> at 0.2 V/Å as depicted in Fig. S8(a) [36], significantly enhanced local polarization can be seen. On the left side of the interface, the polarization intensity is significantly enhanced due to the pronounced polarization activity and atomic migration (Fig. S9 [36]) of Bi and Fe atoms [51] as well as the influence of an applied electric field. The PVDF on the right side of the interface in this case demonstrates significantly enhanced local polarization compared to the single-phase PVDF,



FIG. 6. Microscopic polarization along the z axis in iPP matrix with (a) perovskite fillers, (b) oxide fillers, and (c) 2D layered fillers, averaged along the x-y plane. (d) The polarization charge distribution of BNT/iPP,  $TiO_2/iPP$ , CNO/iPP, where the yellow and blue isosurfaces represent the induced positive and negative charge. Microscopic polarization occurs from areas of positive charge towards regions of negative charge.

thereby indicating the influential role played by the interface. The polarization charge distribution of the BFO/PVDF system in Fig. 5(d) confirms that BFO induces a modulation of the charge distribution within PVDF through a strong interaction, resulting in consistent polarization orientation. Similar phenomena are also observed in the PTO and BNT systems, where an increase in ion disordering within the BTO and STO structures results in a decrease of polarization (see Fig. S9). Compared to perovskite fillers, most oxide fillers exhibit limited polarization activity, albeit with minor polarization peaks near the interface attributed to multiple oxidation states (i.e.,  $Si^{+2}$ , and  $Si^{+3}$  on the SiO<sub>2</sub>/PVDF system) [52], as shown in Fig. 5(b). While among them, the fillers of  $TiO_2$ ,  $SiO_2$ and HfO<sub>2</sub> exhibit relatively high polarization enhancement, exemplified by a PVDF chain polarization magnitude of 10.87  $\mu$ C/cm<sup>2</sup> near the interface of the TiO<sub>2</sub>/PVDF heterostructure. The polarization charge distribution of the TiO<sub>2</sub>/PVDF system is depicted in Fig. 5(d), accompanied by the presence of disordered TiO<sub>2</sub>. Thus, the polarization contribution of the oxide/PVDF system mainly arises from the inherent polarization activity of PVDF itself, with minimal influence from the interface. While for the 2D fillers depicted in Fig. 5(c), the results indicate that the introduction of negatively charged CNO leads to a significantly larger dipole moment in PVDF through charge exchange, as compared to the relatively low polarization enhancement observed in other systems. The polarization charge distribution in Fig. 5(d) reveals a remarkably consistent orientation within the system, and the robust binding of the charges may potentially contribute to an increase in breakdown strength [53]. Therefore, for the polar PVDF matrix, some perovskite fillers with strong ferroelectricity and charged CNO fillers could induce strong interface interaction and thus enhance the local polarization.

The position-dependent-only polarization curves of all heterogeneous systems based on iPP are shown in Fig. 6, where the left side of the gray area corresponds to iPP. The overall polarity of iPP is relatively low due to the limited presence of polar bonds resulting from the similar electronegativity between carbon and hydrogen atoms, as well as the symmetrical chemical structure (the maximum local polarity being  $0.56 \ \mu C/cm^2$  at 0.2 V/Å, refer to Fig. S9(b) [36]). The polarization peaks can be observed on the left side of the interface in almost all components (Fig. 6), with noticeably lower polarization on the right side, indicating that the interfacial polarization of the iPP-based composite system primarily originates from its inorganic fillers. The peak polarization of perovskite fillers, particularly, closely resembles that of pure phase slabs, exemplified by the BTO slab with a polarization peak of 22.3  $\mu$ C/cm<sup>2</sup>, as seen in Fig. S9(c) [36]. The majority of oxides and iPP are typically linear dielectrics, so whether their combination also produces interfacial polarization effects. Our findings reveal that the incorporation of nonpolar oxide fillers such as  $TiO_2$  [refer to Fig. 6(b)] into nonpolar iPP systems leads to a comparable local polarization around the interface. With nonpolar iPP as the matrix, the polarization charge within TiO<sub>2</sub> undergoes redistribution and transfer to the interface region, leading to an augmentation in polarization of multiple atomic layers adjacent to the interface (Figs. 6(d) and S10 [36]). This observed phenomenon may provide an explanation for the enhancement of dielectric constant reported in experiments following the incorporation of ultralow content oxide fillers ( $\leq 1$ vol%) into a linear matrix [54,55]. Finally, a high level of local polarization of CNO was observed in the 2D packing system [Fig. 6(c)], which is consistent with the characteristics observed in the PVDF system, thereby revealing its inherent nature and amplifying its

potential applications. Thus, the induced interfacial polarization may also appear in nonpolar polymer-based composites, and potentially account for their unexpected increase of dielectric properties.

# **IV. CONCLUSIONS**

In polymer nanocomposites, the structure and chemical properties of the interface become crucial when the size of the fillers is reduced to the nanometer or atomic scale. In this study, we have employed DFT calculations to investigate the structure, energy, and electronic properties of nanocomposites composed of various types of fillers and matrices. During the formation of the interface, significant atomic reconstruction occurs in the interfacial region, extending to the interior of the bulk due to periodic absence of surface atoms and lattice mismatches. In terms of interfacial charge redistribution, HfO<sub>2</sub>, TiO<sub>2</sub>, and negatively charged CNO fillers exhibit exceptional performance in facilitating charge transfer. When an electric

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field is applied, it becomes evident that the perovskite material attains local polarization due to its robust polarity. The key observation is that the enhanced local polarization can also be observed when incorporating linear oxide such as  $TiO_2$ , into the linear matrix. Both charge transfer and local polarization outcomes exhibit a reliance on the surface chemistry of the material. This provides direct evidence and theoretical guidance at the electron level for experimentally designing interfaces to optimize heterogeneous structures, thereby enhancing polarization and energy storage properties.

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