Computational framework for polymer synthesis to study dielectric properties using polarizable reactive molecular dynamics

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ABSTRACT

The increased energy and power density required in modern electronics poses a challenge for designing new dielectric polymer materials with high energy density while maintaining low loss at high applied electric fields. Recently, an advanced computational screening method coupled with hierarchical modelling has accelerated the identification of promising high energy density materials. It is well known that the dielectric response of polymeric materials is largely influenced by their phases and local heterogeneous structures as well as operational temperature. Such inputs are crucial to accelerate the design and discovery of potential polymer candidates. However, an efficient computational framework to probe temperature dependence of the dielectric properties of polymers, while incorporating effects controlled by their morphology is still lacking. In this paper, we propose a scalable computational framework based on reactive molecular dynamics with a valence-state aware polarizable charge model, which is capable of handling practically relevant polymer morphologies and simultaneously provide near-quantum accuracy in estimating dielectric properties of various polymer systems. We demonstrate the predictive power of our framework on high energy density polymer systems recently identified through rational experimental-theoretical co-design. Our scalable and automated framework may be used for high-throughput theoretical screenings of combinatorial large design space to identify next-generation high energy density polymer materials.

1. Introduction

Polymers are an important class of materials owing to their chemical resistance, light weight, high processability and ability to act as thermal and electrical insulators. Because of their useful properties, polymer products are ubiquitous in our daily lives and are used in plastics, packaging, military, aerospace and various other fields. In insulation, isolation and electrostatic energy storage technologies, polymers dielectric materials have become mainstays, since they are relatively inexpensive and lighter than ceramic material alternatives. For example, biaxially-oriented polypropylene (BOPP) is currently employed as state-of-the-art polymer dielectric films in electrostatic energy storage capacitors. Despite having high dielectric strength and low dielectric losses, BOPP exhibits relatively low dielectric constant and energy density [1–3]. Therefore, concerted experimental and theoretical efforts have been made to develop a new class of dielectric polymer materials that possess low conduction losses under high electric fields and electrical energy density that can be used in a wide range of applications in modern electronics and electric power systems [4–6].

Due to the rapid advances in machine-learning technologies, the closed-loop cycle consisting of materials synthesis, characterization and computational modeling has been attracting great attentions to accelerate design and discovery of novel materials [7–10]. Advanced computational screening procedures also have been applied and have significantly helped identify important high energy density polymeric materials [11]. Since polymers exist as repeating monomer units, it is possible to express them as a series of strings and store in relational databases [12]. The database can be utilized to create models using machine learning tools to predict relevant polymer properties. This idea has enabled fast computational screening, coupled with hierarchical modelling, to accelerate the identification of promising repeat units to synthesize [11,13]. For instance, polyurea and polythiourea, with –NH-
limited to a few hundred atoms due to the high computational cost. However, system sizes handled by the first-principles approach is for many polyolefins such as polyethylene and polypropylene [21,22]. Critical role of morphology has further been investigated been attributed to the increased spatial distributions in the amorphous samples [21].

On the other hand, significantly higher dielectric constant values have been observed in amorphous phases, in which the vast difference has been observed in amorphous polymer systems, and demonstrated dielectric response subjected to an electric field. Moreover, ReaxPQ+ has been successfully applied to a number of inorganic and organic materials [29], however, the lack of charge-state in the charge state [23] this approach suffers from poor predictions of dielectric response subjected to an electric field.

To circumvent this deficiency, we have developed a scalable computational framework based on a charge-state aware ReaxPQ+ model. The original ReaxPQ model combines all-atoms reactive molecular dynamics (RMD) employing reactive force field (ReaxFF) [24-27] and a recently-proposed polarizable charge model (PQEq) [28]. To study dielectric response under electric field, ReaxPQ+ model was introduced to incorporate the effects from both internal and external electric fields. ReaxPQ+ has been successfully applied to a number of inorganic and organic materials [29], however, the lack of charge-state in the ReaxPQ+ model resulted in time-consuming and laborious parameter tunings, presenting a serious challenge to enable a fully automated high-throughput computational screening for polymer dielectrics. To this goal, we here introduce a charge-state aware ReaxPQ+ model to accurately describe the dielectric responses of amorphous polymers based on the quantum-mechanically informed atomic polarizability. Once model parameters have been developed, our scalable framework predicts dielectric properties of polymers within a small fraction of QM calculations time [29] and handles industrially-relevant polymer chain lengths in a highly-automated fashion. We have applied our model to computationally synthesize amorphous polymer systems, and demonstrated the role of morphological complexity in evaluating the dielectric constant of polymers [21,22]. In addition, we successfully apply the framework validated by the dielectric responses of PDTC-HK511 and TDI-EDR148 to newly identified FPE and DVS-BCB within an experimental accuracy. The subsequent sections present the key components of the framework, obtained dielectric properties and discussions.
2. Methodology

Our framework can be divided into following components: a) synthesis of polymer system, and b) ReaxPQ+ model development and dielectric-constant estimate (Fig. 1). Details of these components are described in subsequent subsections.

2.1. Charge-State aware ReaxPQ+ Model

To take into account the dielectric response to both internal and external electric fields, the ReaxPQ+ model employs the polarizable charge-equilibration scheme called PQEq [28], which in turn introduce core and shell charges to capture the complex interplay between the electronic and ionic dynamics. The potential energy \( E(\{\mathbf{r}_i\}, \{\mathbf{r}_{ij}\}, \{\mathbf{q}_i\}, \{\mathbf{K}_s\}) \) of the system in ReaxPQ+ is represented as a function of relative positions of atomic pairs \( \mathbf{r}_g \), triplets \( \mathbf{r}_{ik} \) and quadruplets \( \mathbf{r}_{ijk} \) atom charges \( q_i \) and bond orders \( BO_{ij} \) between different atomic pairs. In ReaxPQ+, the total charge on \( i \)-th atom is computed based on the contribution from a massless shell \( q_{ic} \) connected to the core \( q_{jc} \) by an isotropic harmonic spring constant \( k_{ic} \) as shown in Fig. 2. The massless shell \( q_{ic} \) has fixed total charge – \( Z_i \) while the core \( q_{jc} \) charge consists of two parts: 1) a dynamically variable atomic charge \( q_j \), and 2) a fixed charge \( Z_j \) compensating the massless shell counterpart.

The atomic charges \( q_i \) are determined by minimizing the total Coulomb energy \( E_{\text{Coulomb}} \) at every step until the electrostatic potentials, \( \partial E_{\text{Coulomb}}/\partial \mathbf{r}_i \), become equal among all atoms. The Coulombic energy is described as

\[
E_{\text{Coulomb}}(\{\mathbf{r}_c, \mathbf{r}_u, \mathbf{q}_c\}) = \sum_i q_i^2 + \sum_{i<j} q_i q_j \left( \frac{1}{r_{ij}} + \frac{2}{3} \varepsilon_0 K_{ic} r_{ic}^2 \right) + \sum_{i<j} \left( C(\mathbf{r}_{ij}) q_i q_j - C(\mathbf{r}_{ij}) q_i Z_i - C(\mathbf{r}_{ij}) q_j Z_j + C(\mathbf{r}_{ij}) Z_i Z_j \right) .
\]

where \( \mathbf{r}_c, \mathbf{r}_u, \mathbf{q}_c \) and \( \mathbf{q}_j \) are the positions of core and shell charges, the electronegativity and the hardness of \( i \)-th atom, respectively. \( \mathbf{r}_{ab} \) \((i,j=1,\ldots, N, a,b=\text{core}(c) \text{ or shell}(s))\) is the charge-charge distances. The electrostatic energy between two Gaussian charges is given in terms of the error function \( C_{ab}(\mathbf{r}_{ab}) \), and the Coulombic interaction is screened using a taper function \( T(r) \) [28]. The shell positions \( \mathbf{r}_u \) subjected to an external electric field \( \mathbf{e} \) is determined

\[
F_{\text{net}} = \frac{\partial}{\partial \mathbf{r}_u} \left( \sum_{a,b} T(\mathbf{r}_{ab}) C_{ab}(\mathbf{r}_{ab}) q_a q_b \right) ,
\]

\[
F_{\text{ext}} = -\frac{\partial}{\partial \mathbf{r}_u} \left( \sum_{a,b} \frac{1}{2} K_{ua} \mathbf{r}_{ua}^2 \right) \text{ and } F_{\text{ext}} = \sum_i q_i \mathbf{e} .
\]

ReaxPQ+ model describes the system polarization via the displacement of Gaussian-shaped shell-charge relative to the core-charge position, which is controlled by two key parameters: the core-charge radius \( R_c \) and the spring constant \( K_s \) between the core–shell charges. A critical component of the ReaxPQ+ model is the choice of atomic polarizability dictated by \( K_s \) which substantially changes depending on their valence charge state. Therefore, the model must be aware of the atomic state to realize accurate prediction of dielectric response as a system. For determining the polarizability of constituent atomic species, we use Hartree-Fock calculations with def2-svp basis sets [30]. Table 1 summarizes the obtained atomic polarizability values with various charge states. The polarizability of neutral atoms is presented as validation in the right-most column, which shows good agreement with values in literature [31]. These polarizability values can be used for initial estimation of \( K_s \).

\[
K_s = C \frac{Z_i}{a}
\]

where \( C \) is a constant conversion factor, \( Z_i \) is the charge on shell attached to core, and \( a \) is the atomic polarizability (Å³), as reported in Table 1.

In addition to the polarizability, an accurate description of atomic charges may improve the estimation of dielectric constants. In this study, we use QM charges throughout our simulations for prediction of dielectric properties. Table S1 in the supporting information presents optimized ReaxPQ-model parameters for the constituent atoms, which are validated using the high-frequency dielectric constant \( \varepsilon_{\infty} \) obtained by Berry-phase method [32, 33].

2.2. Amorphous polymer model creation

The three major steps in the amorphous polymer model creation using TDI-EDR148 as an example system is illustrated in Fig. 3. The initial step involves generating a Simplified Molecular Input Line Entry System (SMILE) string for a polymer structure under consideration. SMILES is a specification in the form of a line notation for describing the structure of chemical species using short ASCII strings. [34] In the second step, Open Babel [35] is used to generate a low-energy structure based on the input SMILES string. Open Babel is a computer software, a chemical expert system mainly used to convert chemical file formats. The obtained polymer-chain structure is relaxed using conjugate-gradient method, followed by RMD simulation at low temperature to relax the bonds, angles, dihedrals and monomer linkages connecting different repeat units together. The final step involves stacking the polymer chains, a series of RMD simulations to consolidate and relax the system to achieve a desired density at a given temperature. Figure S3 shows amorphous structures produced for PDTC-HK511, FPE and DVS-BCB.
Scalable polymer synthesis is realized using a parallel MD engine called RXMD. RXMD employs first principles-informed ReaxFF [24] and a divide-and-conquer strategy to achieve the scalability from desktop computer to supercomputing platforms (Fig. S2). Message Passing Interface (MPI) library is used in data exchanges between processes and inter-process communications [36]. RXMD supports ReaxPQ+ model, thus allowing accurate study of the polarization and dielectric response of materials subjected an electric field.

2.3. Estimation of dielectric constant

The temperature-dependent dielectric constant \( \varepsilon_0(T) \) is calculated using Eq. (4), which consists of the high-frequency dielectric constant \( \varepsilon_\infty \) and the temperature-dependent term,

\[
\varepsilon_0 - \varepsilon_\infty = \frac{\langle \Delta M^2 \rangle}{\Omega k_B T} \tag{4}
\]

where \( \Omega \) is the volume of cell, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( \langle \Delta M^2 \rangle \equiv \langle M^2 \rangle - \langle M \rangle^2 \) is the variance of the total dipole moment \( \mathbf{M}(t) \) over time \( t \). Each component of the total dipole moment is computed as follows:

\[
\mathbf{M}(t) = \langle M_x(t), M_y(t), M_z(t) \rangle = \sum_{j}^{N_{\text{mol}}} \sum_{\alpha}^{N_{\text{atom}}} [x_{\alpha j}(t) - x_{\alpha 0 j}(t)] q_{\alpha j} \tag{5a}
\]

\[
M_x(t) = \sum_{j}^{N_{\text{mol}}} \sum_{\alpha}^{N_{\text{atom}}} [x_{\alpha j}(t) - x_{\alpha 0 j}(t)] q_{\alpha j} \tag{5b}
\]

\[
M_y(t) = \sum_{j}^{N_{\text{mol}}} \sum_{\alpha}^{N_{\text{atom}}} [y_{\alpha j}(t) - y_{\alpha 0 j}(t)] q_{\alpha j} \tag{5c}
\]

Here, \( N_{\text{atom}} \) is the number of atoms in molecule \( j \), \( q_{\alpha j} \) is the charge of atom \( \alpha \), \( r_{\alpha j}(t) \) is the position vector of atom \( \alpha \) with components \( x_{\alpha j}(t) \), \( y_{\alpha j}(t) \), \( z_{\alpha j}(t) \) and \( r_{\alpha 0 j}(t) \) is the position of a reference atom in molecule \( j \) with coordinates \( x_{\alpha 0 j}(t) \), \( y_{\alpha 0 j}(t) \), \( z_{\alpha 0 j}(t) \). We obtain the best estimates for high-frequency dielectric constant \( \varepsilon_\infty \) by further tuning the initial parameter estimates of the ReaxPQ+ model to fit the first-principles Berry-phase method [33,37,38]. The detail of calculation is described in the supporting information (section S5).

Polymer morphologies prepared in the procedure described in Sec. 2.2 have drastic effects on the dielectric constant. To demonstrate these effects, Table S2 compares the calculated dielectric constants for crystalline and amorphous polyethylene (PE).
3. Result and discussion

In this section, we demonstrate our framework on $\varepsilon_0(T)$ of known high density polymers (PDTC-HK511 and TDI-EDR148) and newly identified polymers (DVS-BCB and FPE\cite{17,18}). All amorphous systems are created at experimental density\cite{11,15} following the procedures discussed in Section 2.2.

3.1. Dielectric behavior of TDI-EDR148 and PDTC-HK511

Fig. 4 (a) and (b) show the fluctuation in the total dipole moment $\Delta M(t)$ of the amorphous TDI-EDR148 system at temperatures 100 and 300 K, respectively. We have used a large number of independent RMD trajectories (see Section S4 in supporting information for details) to ensure good statistics without the need of very long-time trajectories. Eq. (5) indicates that the dielectric constant is proportional to the ratio between the variance in the total dipole moment and the system temperature. We observe that the increase of the total dipole moment variance surpasses the temperature term in the amorphous TDI-EDR148 system. We confirm the same trend at various temperatures as well as in amorphous PDTC-HK511 system, see Figs. S3 and S4.

Fig. 5 (a) and (b) show temperature dependence of the dielectric constants of PDTC-HK511 and TDI-EDR148, respectively. The high-frequency dielectric constant $\varepsilon_\infty$ is estimated by ReaxPQ+ scheme using an optimized core–shell radius and atomic polarizability of the constituent atoms. Overall the dielectric constants for these polymer systems reasonably agree well with experiments.\cite{15} The high dielectric constant of these systems may be attributed to the interplay between thermally activated local atomic motions that results in the enhanced fluctuation of molecular dipole moments.\cite{15} Both PDTC-HK511 and TDI-EDR148 are rigid-base polymer containing a benzene ring and a flexible etheramine in the backbone. This flexible segment within the backbone gives an extra ability of local chain movement thus increasing the dielectric constant, which may facilitate further polarization when subjected to an external electric field.\cite{15}.

3.2. Dielectric behavior of DVS-BCB and FPE

DVS-BCB and FPE are promising materials that exhibit high dielectric constant values and high thermal stability.\cite{17,18} DVS-BCB is used in preparation of commercially available resins for multichip modules and four-level GaAs interconnect circuits.\cite{17} DVS-BCB and FPE both have high glass transition temperature, thus allowing graceful failure and roll-to-roll production capabilities.\cite{39} Following the previously

![Fig. 5. Dielectric constants of (a) PDTC-HK511 and (b) TDI-EDR148 polymer systems (blue dots) as a function of temperature. The increasing trend as well as predicted values show a good agreement with experimental values (shown in red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 6. Dielectric constants of (a) DVS-BCB and (b) FPE polymer systems as a function of temperature. The predicted values show a good agreement with experiments\cite{16,17,40–44} .](image)
described procedures, we have computed the temperature-dependence in dielectric constant \(\varepsilon_0(T)\) based on samples taken from a large number of RMD trajectories. Fig. 6 shows the temperature-dependent dielectric constant of amorphous DVS-BCB and FPE systems. Overall, the obtained dielectric constants agree well with experiments. [17,18,40–44].

4. Conclusion

In conclusion, we have developed a scalable computational framework to evaluate the temperature-dependent dielectric responses of amorphous polymer. The seamless creation of amorphous polymer structure realized by SMILES strings, Open Babel, and RXMD allowing researchers to explore the vast parameter space of high energy polymer design with a highly automated fashion. Equipped with the scalable parallel all-atom RMD simulation engine, it is possible to incorporate complex repeat units with industry-relevant chain lengths. The model parameters, such as atomic polarizability, core–shell charges and radii, are extensively optimized and validated by experiments and first-principle calculations using the high-frequency as well as temperature-dependent dielectric constants. Our computational framework has been successfully applied to the recently identified four high energy density polymers, PDTC-HX511, DVB-EDR148, DVS-BCB and FPE, and revealed that the thermally activated flexible segment motion in polymer chains facilitates the fluctuation of the molecular dipole moments. The obtained dielectric constants as well as its increasing trend quantitatively agree with the experiments. The computational framework presented here for the first time realizes high throughput theoretical screenings incorporating several key parameters in the high energy density polymer design. Therefore, combined with efficient experimental synthesis and characterization, our framework is expected to accelerate the discovery of next-generation high energy density polymer and device development.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.commatsci.2023.112340.

References

A. Hellweg, D. Rappoport, Development of new auxiliary basis functions of the Karlsruhe segmented contracted basis sets including diffuse basis functions (def2-SVPD, def2-TZVPPD, and def2-QVPPD) for RI-MP2 and RI-CC calculations, PCCP 17 (2) (2015) 1010–1017.


