

Supporting Information

Revealing the Mechanism of Sodium Diffusion in Na_xFePO_4 Using an Improved Force Field

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S1. Parameter Optimization with *potfit*: additional details

The software *potfit*[1, 2] determines the optimal set of parameters for a given force field by minimizing the error in the forces, stresses and energies with respect to a set of structural configurations of the system. For a training dataset consisting of M configurations, the scoring function is given by

$$Z = \sum_{m=1}^M \left[3\omega_e (e_m - e_m^0)^2 + \frac{1}{2}\omega_s \sum_{l=1}^6 (s_{m,l} - s_{m,l}^0)^2 + \sum_{n=1}^{3N_m} (f_{m,n} - f_{m,n}^0)^2 \right], \quad (\text{S1})$$

where N_m is the number of particles in configuration m . $\{e_m\}$, $\{s_{m,l}, l = 1, \dots, 6\}$ and $\{f_{m,n}, n = 1, \dots, 3N_m\}$ are the energies, stresses and forces obtained with the trial force field, respectively. The superindex 0 denote the reference values from the training dataset. ω_e and ω_s are user-defined weights to balance the amount of available information for each quantity.

potfit combines stochastic simulated annealing [1, 2] and a conjugate-gradient-like deterministic algorithm to perform the optimization [3]. In the simulated annealing algorithm, we found that tuning some parameters hard-coded in the software improved our optimal parameters search [4]:

- N_s = number trials for each parameter, before adapting the step length. This parameter was increased from 25 to 50.
- N_T = maximum number of adaptations for the step length before decreasing the temperature. This parameter was increased from 2500 to 3500.

- T_{new}/T_{old} = Reduction factor in the temperature. This parameter was increased from 0.8 to 0.9.

A more detailed description of the role of these parameters can be found in the online reference at <https://www.potfit.net/wiki/doku.php?id=algorithms:simann>.

The fitting quality is determined by the root mean square (rms) errors. For a dataset in which each configuration contains N atoms, the root mean square (rms) errors of the energies, force and stresses are given by

$$\Delta F_e = \sqrt{\frac{Z_e}{3MN}}, \quad \Delta F_s = \sqrt{\frac{2Z_s}{MN}}, \quad \Delta F_f = \sqrt{\frac{Z_f}{MN}}, \quad (\text{S2})$$

where Z_e , Z_s and Z_f are the first, second and third terms on the right hand side of eq. S1, respectively.

The weights used in equation S1 were set to $\omega_e = 1$ and $\omega_s = 50$. This combination provided the best balance between force, stress and energy error minimization.

S2. Specifying the location of the shells for parameter estimation

Since the core-shell unit is simply a construct to introduce polarizability within an empirical force field, the *ab initio* dataset does not provide information on how to specify the core and shell coordinates. For the core, a sensible solution consists in setting its position to that of the actual ion, because the core carries most of the core-shell unit mass. For the shell, its position should be selected in such a way that the total force on it is zero. In previous works, the shell positions were chosen by minimizing the forces acting on them using the initial guess on the force field parameters. Then, during the optimization, their positions were readjusted from time to time as the force field parameters change. [5, 6]. In our experience, this leads to a parameter set that might not be optimal.

In this work, we propose a more consistent approach to treat the shells positions. We fix the spring constant and charge distribution (X and Y) for all core-shell units prior to starting the parameter estimation. Then, given that dispersion interactions on core-shell unit l are assigned to the shell only, the total force in core l , $\vec{F}_{l,core}$, becomes

$$\vec{F}_{l,core} = \vec{F}_{l,core}^{elec} + k_l(\vec{r}_{l,shell} - \vec{r}_{l,core}), \quad (\text{S3})$$

where $\vec{F}_{l,core}^{elec}$ is the electrostatic force on core l , and $\vec{r}_{l,core}$ and $\vec{r}_{l,shell}$ are the respective core and shell positions. Since the force on the shell must in principle be zero, $\vec{F}_{l,core}$ should correspond to the force on the l th ion $\vec{F}_{l,ion}$, estimated from DFT. Hence, the shells must be allocated such that

$$\vec{r}_{l,shell} - \vec{r}_{l,core} + (\vec{F}_{l,ion} - \vec{F}_{l,core}^{elec})/k_l = 0, \quad \text{for } l = 1, \dots, L. \quad (\text{S4})$$

$\vec{F}_{l,core}^{elec}$ depends only on the charge distribution and atom positions. Hence, expression (S4) represents a system of $3L$ force field-independent equations and $3L$ unknown variables for the shells coordinates. In this work, the charge distribution and spring constants were left as proposed by Whiteside et al. [7]. The equations in (S4) were solved by a simple fixed-point iteration scheme. A schematic of the method is depicted in Figure S1.

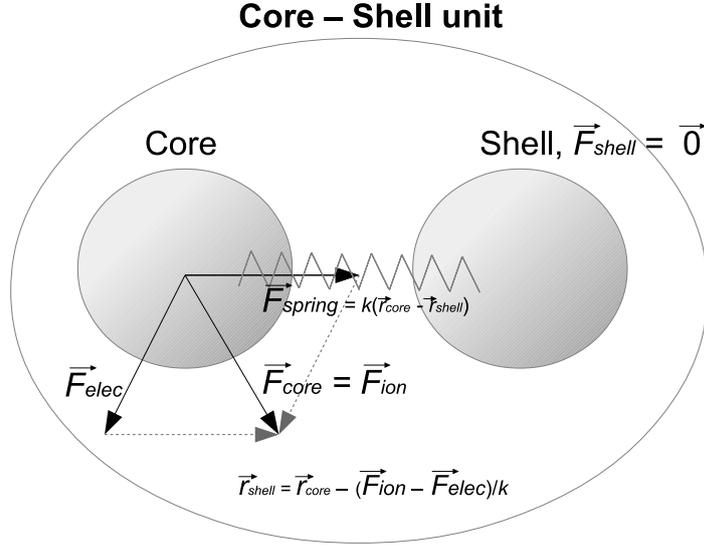


Figure S1: Correct positioning of the shell within a core-shell unit. If the charges and the spring constant k are set, the fact that dispersive forces do not act on the core uniquely determine the exact position for the shell.

S3. Comparison between Whiteside-ff and Na_xFePO_4 -ff at $x = 0.58$

One of the advantages of the new force field is its ability to simulate materials with varying sodium concentrations. Removing Na^+ ions from a NaFePO_4 crystal results in increased repulsion between the oxygen shells surrounding the newly created vacancies. This leads to expansion of the lattice that can cause numerical instability in molecular dynamics simulations. Figure S2 shows the radial distribution functions for phosphorous atoms, $g_{P-P}(r)$, in the $\text{Na}_{0.58}\text{FePO}_4$ system at 300 K after 0 ps and 10 ps of simulation using the NaFePO_4 -ff and Whiteside-ff. The figure illustrates how the $(\text{PO}_4)^{3-}$ tetrahedrals displace over time when using the Whiteside-ff in a Na_xFePO_4 system with $x < 1$. The dashed line corresponds to the initial positions, which is the same for both force fields. However, after 10 ps of simulation, there is a distortion in the position of the peaks for Whiteside-ff with respect to the initial $g_{P-P}(r)$, evidencing the additional repulsion between oxygens of adjacent tetrahedrals when a Na^+ ion is removed. This anomalous effect is not observed with Na_xFePO_4 -ff due to the reoptimized parameters.

S4. Volume divergence observed with Whiteside-ff, Na_xFePO_4 -ff and DFT

Figure S3 shows the relative volume divergence for a range of concentrations at $T=300$ K with respect to experimental results from Ref. 8. We define this divergence as $|V - V_{exp}|/V_{exp}$, where V is the calculated unit cell volume and V_{exp} the experimental one. They were obtained using the two different force fields, combined with RSM-GSHMC. The forcefield developed in this study, i.e

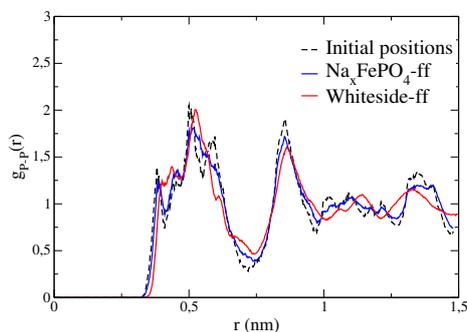


Figure S2: Radial distribution functions for phosphorous atoms in a $\text{Na}_{0.58}\text{FePO}_4$ system after 10 ps at 300 K.

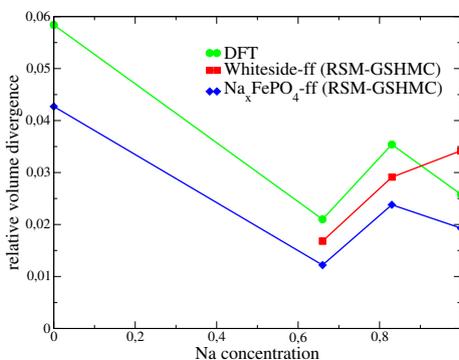


Figure S3: Relative volume divergence with respect to experimental results [8] in a Na_xFePO_4 system observed using DFT and atomistic simulations combined with two different force fields.

$\text{Na}_x\text{FePO}_4\text{-ff}$, is closer to the experiments than Whiteside-ff and DFT. In the case of DFT, the divergence is likely because experiments were performed at 300 K, while DFT data were obtained at 0 K. However, the trends demonstrated by DFT and our force-fields are very similar, which is not the case with Whiteside-ff.

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