ELECTRODE

ELECTRODE: An electrochemistry package for LAMMPS

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The constant potential method (CPM) is a commonly used tool to address challenges at the solid-liquid interface at conducting electrodes in molecular dynamics (MD) and can be used, for example, to model the behavior of ionic liquids or water in salt electrolytes in supercapacitors and batteries. CPM achieves this by updating charges of individual electrode atoms according to the applied electric potential and the (time-dependent) local electrolyte structure. Here we present a feature-rich CPM implementation for the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), which includes, in addition, a related atom-wise constrained charge method and a thermo-potentiostat. Moreover, features such as a finite-field approach, multiple corrections for non-periodic boundary conditions of the particle-particle particle-mesh solver (P³M), and a Thomas-Fermi model for using non-ideal metals as electrodes are included. We demonstrate the capabilities of this implementation for a simple electrical double layer capacitor (EDL), for which we have studied the effects on charging time using the different approaches. To confirm the one-dimensional correction, we estimated the vacuum capacitance of a double-cylindrical capacitor and compared it to the analytical result. In summary, the ELECTRODE package enables efficient electrochemical simulations using state-of-the-art methods that open up the possibility of simulating heterogeneous electrodes or electrodes consisting of isolated carbon nanotubes to investigate the influence of curvature on capacitance in more detail.

I. INTRODUCTION

The constant potential method (CPM)1–2 is a popular tool in molecular dynamics (MD) for modeling metal electrodes by dynamically updating individual charges on electrode atoms. CPM allows MD simulations to faithfully reproduce the behavior of electrolytes near electrodes, in particular the correlation between thermal electrolyte fluctuations near the electrode and the induced charge polarization of the electrode, while obtaining a realistic picture of the electrical double layer. Alternatively, image charge methods3,4 are commonly used to enforce a constant potential for planar electrodes. Apart from this, another much simpler way to model electrodes is to assign a uniform charge to each electrode. While treating the electrodes as uniformly charged, structureless, or atomically resolved walls is sufficient to determine the equilibrium electrolyte behavior near planar electrodes at low charge densities and is still common practice, several studies have emphasized the importance of considering the polarization of the electrodes by the ions and molecules at the interfaces5–8. If any of the above criteria are violated or the dynamical behavior of the system is of interest, CPM MD provides results that are significantly different from those obtained with uniformly charged electrodes9. Near highly charged planar electrodes10–12 and non-planar electrodes (such as curved substrates or nanoporous carbons)9,13–18, the spatially-specific charge polarization observed in CPM MD or even in Monte Carlo simulations19 significantly affects the structure of nearby electrolyte particles. CPM MD also captures the temporal response, in the build-up and dissipation of electric layers, to electrode charges, and thereby allows realistic capacitor charging and discharging curves to be generated in silico9,20–22.

Here, we present a package for treating electrodes in MD simulations which interfaces with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)23. It makes use of the highly parallelized and efficient computational infrastructure of LAMMPS and furthermore allows interaction with many other packages and features which are already available in LAMMPS. This work builds in part on an earlier work in which we showed how a particle-particle particle-mesh (P³M)-based calculation makes the electrostatic calculations of a CPM simulation much more efficient24. In addition to a few modifications of the CPM, moreover, this implementation provides a constrained charge method (CCM) and a thermo-potentiostat (TP)25. In order to capture the electronic response of non-ideal metals, a Thomas-Fermi (TF) model26 is included. Both an Ewald and a P³M k-space solver are available for various constraints of the periodicity of the systems, such as infinite slabs, wires or fully 3D periodic systems. This package also implements the closely-related finite field (FF)27 and finite displacement (FD)28 methods, which extend CPM MD to fully periodic boundary conditions for increased computational efficiency.

This paper documents the latest version of the ELECTRODE package and outlines future development plans. The list of new features are presented in Section II including a brief description of their theoretical background. In Section III, we summarize the concept of CPM MD using data generated from CPM MD production runs of various kinds and describe when its use is necessary followed by an outline of future directions for development.
II. FEATURES

A. Constant potential method

A distinctive feature of CPM MD is the calculation of electrode charges, such that the electrodes are maintained at a desired electrostatic potential. Usually the Coulombic contribution of the electrodes $U_{\text{elec}}$ are written in terms of an electrode charge vector $\mathbf{q}$ comprising all electrode charges as

$$U_{\text{elec}}(\{\mathbf{r}\}, \mathbf{q}) = \frac{1}{2} \mathbf{q}^T \mathbf{A} \mathbf{q} - \mathbf{b}^T(\{\mathbf{r}\}) \mathbf{q} - \mathbf{v}^T \mathbf{q} \quad (1)$$

with a matrix $\mathbf{A}$, and vectors $\mathbf{b}$ and $\mathbf{v}$, where $\mathbf{b}$ depends on the electrolyte positions $\{\mathbf{r}\}$. The applied potential $\mathbf{v}$ has an entry for every electrode atom in this general form. The elastance matrix $\mathbf{A}$ represents the Coulombic interactions between electrode particles. Under the assumption that the electrodes do not move, $\mathbf{A}$ can be pre-computed, allowing significant computational savings. The electrolyte vector $\mathbf{b}(\{\mathbf{r}\})$ represents the electrostatic potential on each electrode particle due to the electrolyte particles, as a function of their positions.

At each step $\mathbf{q}$ is updated to minimize the Coulombic energy contribution $U_{\text{elec}}$, possibly subject to additional constraints. The desired energy-minimizing charge vector $\mathbf{q}^*$ is straightforward to calculate:

$$\mathbf{q}^* = \mathbf{A}^{-1} [\mathbf{b}(\{\mathbf{r}\}) + \mathbf{v}] \quad (2)$$

The main computational burden is the calculation of $\mathbf{b}(\{\mathbf{r}\})$ at every time step which is necessary due to the motion of the electrolyte. The primary purpose of the ELECTRODE package is to carry out this additional calculation efficiently and update the electrode charges accordingly. Alternatively, the electrode charges can be obtained by employing the conjugate gradient method to solve the minimization problem without a matrix inversion. Yet another approach is to treat the electrode charges as additional coordinates and perform mass-zero constrained dynamics for them$^{29}$. For more information on the CPM MD approach, see the excellent and thorough review of current electrode-electrolyte simulations in Scalfi et al.$^{30}$.

In MD with periodic boundary conditions, the simulation cell ideally comprises zero total charge. As described by Scalfi et al.$^{31}$, this constraint could be imposed by using the symmetric matrix

$$\mathbf{S} \equiv \mathbf{A}^{-1} - \frac{\mathbf{A}^{-1} \mathbf{e} \mathbf{e}^T \mathbf{A}^{-1}}{\mathbf{e}^T \mathbf{A}^{-1} \mathbf{e}}, \quad \mathbf{e} = (1, \ldots, 1) \quad (3)$$

as capacitance matrix instead of $\mathbf{A}^{-1}$.

In order to model non-ideal metallic electrodes a semiclassical TF model has been recently presented by Scalfi et al.$^{28}$. We have implemented this promising approach in our ELECTRODE package, since it is very similar to the self-interaction correction of the Ewald summation$^{12}$ and contains only a single summation over the electrode atoms. An interesting alternative to effectively model a wide range of materials between insulator and ideal metal was proposed by Schlaich et al.$^{33}$ and involves the use of a virtual TF fluid within the electrodes. However, a virtual TF fluid approach appears to be computationally more expensive.

B. Simulating an arbitrary number of electrodes

Typically, CPM MD is performed with two electrodes which means there are only two possible values for each of the $n$ entries of the potential in Eq. 1, i.e. $v_i \in \{v_{\text{top}}, v_{\text{bot}}\}$. In the ELECTRODE package an arbitrary number $N$ of electrodes is allowed with every electrode atom belonging to exactly one electrode. We define an electrode-wise indicator vector $\mathbf{g}_\alpha$ for every electrode $\alpha$ with $n$ entries which are equal to 1 if the respective electrode particle belongs to that electrode and 0 otherwise. The indicator matrix

$$\mathbf{G} = [\mathbf{g}_1 \mathbf{g}_2 \ldots \mathbf{g}_N] \quad (4)$$

comprising the indicator vectors of all $N$ electrodes allows us to connect electrode-wise quantities to particle-wise quantities. As an example we define $\tilde{\mathbf{v}}$ as the electrode-wise potential and use it to write the potential $\mathbf{v} = G \tilde{\mathbf{v}}$. In the following a tilde will be used for electrode-wise quantities. Using this notation, the energy-minimizing charges $\mathbf{q}^*$ for a given set of electrode-potentials is

$$\mathbf{q}^* = \mathbf{S}(\mathbf{b} + \mathbf{v}) = \mathbf{S} \mathbf{b} + \mathbf{S} G \tilde{\mathbf{v}} \quad (5)$$

C. Simulating electrodes at specified total charge

In the constrained charge method (CCM), the electrode-wise total charge $\tilde{\mathbf{q}}^*$ is set, representing an open circuit condition. This type of simulation has recently been attempted as a variation of the finite-field method (described in Section II F)$^{28}$. Therein, it was found that the open circuit system, with the total charge being ramped up or down over time, could be considered as computational amperometry, and a faster non-equilibrium response was observed.

Working with the raw capacitance matrix $\mathbf{A}^{-1}$, rather than the symmetrized matrix $\mathbf{S}$ (since charge neutrality is explicitly enforced by appropriate choice of $\tilde{\mathbf{q}}^*$), we have:

$$\tilde{\mathbf{q}}^* = \mathbf{G}^T \mathbf{q}^* = \mathbf{G}^T \mathbf{A}^{-1} \mathbf{b} + \mathbf{G}^T \mathbf{A}^{-1} G \tilde{\mathbf{v}} = \tilde{\mathbf{q}}_b + \tilde{\mathbf{C}} \tilde{\mathbf{v}} \quad (6)$$

$\tilde{\mathbf{q}}_b$ defines the total charge each electrode would have at zero potential, and $\tilde{\mathbf{C}}$ is the electrode-wise capacitance matrix. Subsequent to estimate $\tilde{\mathbf{q}}_b$, Eq. 6 is solved for $\tilde{\mathbf{v}}$ which is then applied using the CPM. This results in an energy minimization w.r.t. the charge distribution with a constraint on the total electrode charges. Analogous to how constant volume and constant pressure simulations can be thermodynamically equivalent, CCM and CPM simulations will give the same capacitances under suitable conditions. However, a thorough proof of that assumption is out of scope of this work and will be discussed in an upcoming work.

D. Simulating electrodes with a thermo-potentiostat

In a recent publication, Deißenbeck et al.$^{25}$ have presented an thermo-potentiostat (TP) that takes into account the fluctuation-dissipation relation of electrode charges at a given
voltage and temperature in an electronic circuit. They have also provided a TP implementation based on a uniform charge distribution using the scripting capability of LAMMPS. The ELECTRODE package provides an implementation that minimizes energy with respect to charge distribution and conforms to the formalism described in Deißenbeck et al.\textsuperscript{25}.

Our TP approach is currently limited to only two electrodes and instead of a vector of applied potentials \( \mathbf{v} \) a potential difference \( \Delta v = v_{\text{top}} - v_{\text{bot}} \) between two electrodes is used. At every time step the potential difference \( \Delta v(t) \) between the two electrodes is evaluated to find the new capacitor charge according to

\[
q(t + \Delta t) = q(t) - C_0 [\Delta v(t) - \Delta v_0] \left( 1 - e^{-\Delta t/\tau_e} \right) + X \sqrt{k_B T_e C_0} \left( 1 - e^{-2\Delta t/\tau_e} \right). \tag{7}
\]

Here, \( \tau_e \) and \( T_e \) are parameters of the TP and \( X \) is a normally distributed random number with a mean of 0 and a standard deviation of 1. The vacuum capacitance \( C_0 \) is obtained from the capacitance matrix\textsuperscript{31} and the effective potential \( \Delta v(t) \) is computed from the electrode charges and the electrolyte configuration (cf. Eq. 6). Hence, all required quantities for Eq. 7 are available within the framework of the CPM. The obtained capacitor charge \( q(t + \Delta t) \) is applied using the protocol outlined in Section II.C.

E. Simulations with different periodicity

The Ewald summation assumes commonly periodic boundary conditions in all three directions and has to be modified for systems with slab and wire geometries. As shown by Smith\textsuperscript{34}, a regular 3D Ewald summation for slab-like systems, which are periodic in the xy-plane but confined in z-direction, results in a so-called “dipole term” which was subsequently used for correcting the infinite boundary artifact of slab-like systems\textsuperscript{35}. This is known as the EW3DC method and is implemented in many MD codes including LAMMPS\textsuperscript{23}. Alternatively, recently Hu\textsuperscript{32} and earlier also others\textsuperscript{36-38} have shown that the infinite boundary contribution in slab-like geometries can be solved in an exact form. This rarely implemented EW2D solver is another cornerstone of this implementation.

Just like slab-like geometries, systems with only one periodic dimension require an appropriate treatment of the long-range electrostatic interactions. As shown by Bródká and Śliwiński\textsuperscript{39} the approach of Smith\textsuperscript{34} can be extended for an infinitely extended prism or wire summation. Corrections for one-dimensional periodic systems are rarely implemented, with the exception of the here presented ELECTRODE package, in established codes and, more crucially, to our knowledge those have not yet been implemented anywhere in combination with a CPM. More details on how this needs to be adapted for a CPM is given in the SI.

F. Simulating electrodes with the finite field method

In the finite field (FF) method\textsuperscript{27}, the potential difference between two electrodes is not directly specified using the applied potential \( \mathbf{v} \). Instead, the simulation cell is treated as periodic in the \( z \) direction, i.e., without adding the otherwise required artificial vacuum between the slabs. The FF method allows for very efficient simulations of infinite electrode slabs, since no additional vacuum is required. However, complexly shaped electrodes or electrodes with a one-dimensional periodicity cannot be simulated with the FF method.

A potential difference \( \Delta v_0 = v_{\text{top}} - v_{\text{bot}} \), between two electrodes, denoted here top and bottom, is created in the FF method by introducing a \( z \)-directed electric (polarization) field of magnitude \(-\Delta v_0/L_z\), creating a discontinuity of \( \Delta v_0 \) across the periodic \( z \) boundary (and thus between the two electrodes on either side of the slab). In this formulation, the electrode Coulombic energy is

\[
U_{\text{elec}} = \frac{1}{2} \mathbf{q}^T \mathbf{A} \mathbf{q} - \mathbf{b}^T (\{\mathbf{r}\}) \mathbf{q} + \Delta v_0 \mathbf{\zeta}^T \mathbf{q}. \tag{8}
\]

Here \( \mathbf{\zeta} \) is a vector containing the normalized \( z \)-positions of each electrode atom, namely \( \{z/L_z\} \) with an offset for the bottom electrode to make the system symmetric along the \( z \)-direction, replicating the conductor-centered supercell in Ref. 27. The energy-minimizing charge \( \mathbf{q}^* \) in this model is

\[
\mathbf{q}^* = \mathbf{S} [b(\{\mathbf{r}\})] + \Delta v_0 \mathbf{\zeta}^T \mathbf{q} \tag{9}
\]

which is analogous to Eq. 2, replacing \( \mathbf{v} \) with \(-\Delta v_0 \mathbf{\zeta}\).

III. RESULTS AND DISCUSSION

A. Charging times

In order to demonstrate the importance of the chosen electrode model for charging dynamics, charging times are computed and illustrated in Fig. 1 for a simple capacitor employing a selection of the introduced methods. The capacitor is adapted from an example in the MetalWalls repository\textsuperscript{40} and comprises a saline solution between two gold electrodes with three layers each. Fig. 1 compares CPM, CCM and TP, the latter with a time constant \( \tau_e = 100 \text{ fs} \) to each other and their uniformly charged counterparts. For the uniform variants, the charges are always evenly distributed across the inner layers of the electrodes. Moreover, Fig. 1 features a CPM setup with the TF approach with \( f_{TF} = 1 \) A.

When CPM MD is initially turned on the charge induced on both electrodes is very small, since the capacitance of the electrode pair in vacuo is small\textsuperscript{24,31}. However, the electrode charges induce the formation of electric layers in the electrolyte, which in turn induce additional charge on the electrode. CPM MD thus models the process of charging up a dielectric capacitor physically correct, and the charging-discharging curves obtained from CPM MD can be used to fit parameters for macroscopically equivalent electrical circuits\textsuperscript{41}. Thus, charging times \( \tau \) are obtained by fitting an
FIG. 1. Charging time constants \( \tau \) and empirical standard deviation employing different CPM approaches as denoted on the y-axis. Inset shows the model system used to compare the different approaches, consisting of an aqueous NaCl electrolyte in contact with a gold surface. Note the different time scales of \( \tau \) for CCM and CPM approaches.

The exponential charging function \( M^{eq}_z[1 - \exp(-t/\tau)] \) to the \( z \)-component of the electrolyte dipole. \( M^{eq}_z \) is the extrapolated equilibrium dipole which is reached after a sufficiently long charging time.

The results of the calculations are shown in Fig. 1. The charging constants obtained with the CCM are about two orders of magnitude smaller than for the potential based methods which is a well known effect\(^{9,42} \). Charging times for uniform methods are very close to their counterparts which is consistent with previous studies that found only small differences between a heterogeneous and uniform CPM at low voltages for simple planar electrodes\(^{10} \). Quite noticeable is that the TF approach leads to a significantly lower charging constant and also a 20% smaller equilibrium dipole compared to a pure CPM with \( l_{TF} = 0 \).

The impact of the TF-length on the charging time was investigated in more detail in Fig. 2a which shows a clear trend towards faster charging for an increasing TF length. On the other hand the use of a TP leads to larger charging constants. This is expected because the TP includes a dissipation term (cf. Eq. 7) which leads to a delayed response in terms of weaker coupling to the external reservoir via \( \tau_v \). As shown in Fig. 2b, the time constant has a strong effect on the charging dynamics. This could potentially be used to model a resistor with resistance \( R \) outside of the capacitor via \( \tau_v = RC_0 \).

For a comparison between the equilibrium conditions of the CPM and CCM we compare the capacitance per area from the fitted equilibrium charges and voltages. The obtained values of 2.65 \( \mu Fcm^{-2} \) and 2.60 \( \mu Fcm^{-2} \) for the CPM and CCM respectively differ by only 2\%. However, a thorough sampling is crucial for a reliable estimate of the differential capacitance, and thus we attribute this small difference between the two ensembles to insufficient sampling caused by the relatively short simulation times.

FIG. 2. (a) Charging time constants \( \tau \) for the CPM with varying Thomas-Fermi length \( l_{TF} \). \( l_{TF} = 0 \) is identical with the standard CPM in Fig. 1. (b) Charging time constants \( \tau \) for the TP with different TP time constants \( \tau_v \).

B. Cylindrical capacitor

As a sanity check of our approach for systems which are periodic in just one dimension, capacitances of wire geometries, represented by a double walled carbon nanotube (DWCNT), are compared to analytical results for structureless cylindrical capacitors. At large radii the atomic structure of the DWCNT should have a negligible effect and thus the results should approach those of structureless capacitors. In both cases a small cylinder is surrounded non eccentricly by a larger one with radii \( R_1 \) and \( R_2 \), respectively (cf. inset of Fig. 3). The vacuum capacitance \( C_0 \) of the DWCNT can be calculated from the electrode-wise capacitance \( C^{31} \). The analytical line capacitance for a given ratio of the radii is:

\[
C^{(wire)}_0 \cdot l^{-1} = \ln(R_2/R_1)^{-1} / 2
\]

in which \( l \) is the length of the simulation box in the periodic dimension. As shown in Fig. 3 for various fixed ratios of the inner and outer tubes, the capacitance of a DWCNT does indeed converge to that of a structureless cylindrical capacitor at large radii compared to the bond length between carbon atoms \( d_{CC} \).

IV. CONCLUSIONS

We present the ELECTRODE package as an efficient implementation of the constant potential method (CPM) and closely related methods for the popular LAMMPS simulation environment. While the main goal was to bring together the many different approaches for electrochemical simulations into one package and ensure that they are handled in the most computationally efficient manner, we also implemented a number of new features whose capabilities and full potential have hardly been explored yet. Other methods, such as the EW2D summation and a wire correction for systems periodic in one dimension were additionally implemented in this process and work independently of the CPM. Recent improvements to the CPM such as the finite field (FF) method and a
The source code of the ELECTRODE package is made available under github.com/robeme/lammps/tree/electrode and is intended to be incorporated in the LAMMPS repository.

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DATA AVAILABILITY STATEMENT

See supplementary material for details on the boundary corrections, a description of the package interface to LAMMPS and an overview of the implemented classes.

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SUPPLEMENTARY MATERIAL

See supplementary material for details on the boundary corrections, a description of the package interface to LAMMPS and an overview of the implemented classes.

FIG. 3. Dielectric capacitance of cylindrical capacitors for fixed ratios of $R_1/R_2$ with $R_1$ the inner and $R_2$ the outer tube radii. Results for double walled carbon nanotubes computed with MD are indicated as lines. Analytical results for a structureless equivalent system are denoted by marks. The difference between the radii is given relative to the characteristic bond length $d_{CC}$ between carbon atoms in graphene.

Thomas-Fermi (TF) model are included and have been compared for consistency to results found in the literature.

The results so far demonstrate the capabilities of the ELECTRODE package to efficiently simulate even rather large or unusual systems such as an infinitely long charged wire. Moreover, the charging process of a capacitor with aqueous NaCl electrolyte illustrates vividly the differences between the range of methods introduced here and used to estimate the electrode charges. For a capacitor composed of DWCNT the vacuum capacitance agrees well within the limit of the analytical result of a structureless cylindrical capacitor and enables the investigation of curvature-dependent effects of more rigorously in the future by avoiding interactions between wires through the periodic images.

While the package is in a stable state, the development is ongoing and will include in the future features like a conjugate gradient or compatibility to TIP4P water models.
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SI - ELECTRODE: An electrochemistry package for LAMMPS

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I. BOUNDARY CORRECTIONS

For a system with slab geometry, a dipole correction

\[ J^{(\text{slab})}(M) = \frac{2\pi}{V} M_z^2 \]  

(1)
to the Coulombic energy can be used. \( M_z \) is the \( z \)-component of the dipole of the simulation cell. For a system with a wire geometry, with a periodic boundary condition in \( z \)-direction but not in the \( xy \)-plane, the dipole correction in Eq. 1 can be extended:

\[ J^{(\text{wire})}(M) = \frac{\pi}{V} \left( M_x^2 + M_y^2 \right) \]  

(2)

Here, \( z \) is the periodic dimension and \( M_x \) and \( M_y \) are the respective component of the total dipole of the unit cell.

The boundary corrections can be included in the constant potential method (CPM) formalism with ease by splitting the dipole components into their electrode and electrolyte contribution:

\[ J^{(\text{slab})} = \frac{2\pi}{V} \left[ (M_{z}^{\text{electrode}})^2 + 2M_{z}^{\text{electrode}}M_{z}^{\text{electrolyte}} + (M_{z}^{\text{electrolyte}})^2 \right] = \frac{2\pi}{V} \left[ \sum_{ij} z_i q_i z_j q_j + 2M_{z}^{\text{electrolyte}} \sum_{i} z_i q_i + (M_{z}^{\text{electrolyte}})^2 \right] \]  

(3)

This way dipole corrections fit into the linear form of the Coulombic energy that is used in the CPM and the computational effort for the electrode-electrolyte interaction scales linearly with the number of particles.

II. PACKAGE OVERVIEW

A. Interface

The ELECTRODE package is designed as an add-on to Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) and integrates seamlessly with most molecular dynamics (MD) simulations carried out with that package. The user must first select one of two long-range Coulombic solvers (“kspace styles” in LAMMPS terminology) included in ELECTRODE, which implement either Ewald summation\(^4\) (ewald/electrode) or mesh-based summation\(^5,6\) (pppm/electrode) with additional methods to compute long-range contributions to the matrix \( A \) and vector \( b \).

The user can then include the following command in the simulation script:
fix <ID> <group> electrode/<mode> <value> <eta>

followed by optional keywords. Mandatory inputs are as follows:

- ID is used for identification of the fix. The applied potential for each electrode is available via $f_{<ID>}[<x>]$.

- group specifies the LAMMPS group of particles to which the potential or charge value will be applied with CPM or constrained charge method (CCM), respectively; additional groups are specified with the couple keyword.

- mode chooses which of the following variants is performed:
  
  - conp: constant potential
  - conq: constrained charge
  - thermo: thermo-potentiostat (TP)$^7$

- eta specifies the reciprocal width of Gaussian smearing applied to the electrode charges.

The following optional keywords are available:

- couple <group-x> <value> allows additional groups to be specified as an electrode. Can be used multiple times to specify more than two electrodes.

- etypes <types> allows users to optionally specify atom types exclusive to the electrode, so that LAMMPS can provide optimized neighborlists for faster calculations.

- symm [on/off] allows users to enforce charge neutrality for the electrodes via matrix pre-projection (cf. Eq. 3).

- ffield [on/off] allows users to turn on or off the finite-field implementation$^8,9$. ELECTRODE automatically creates the electric field required to polarize the simulation box.

- [write/read]_[mat/inv] <path> specifies a file path for input or output of the elastance or capacitance matrix.

- temp <T-v> <tau-v> specifies the parameters $T_v$ and $\tau_v$ in Eq. 7. Only available when using the TP.
FIG. S1. Overview of the package. Each box represents a parent class. Implementations of the respective class are listed with bullet points. Essential methods of each class are listed and their interactions are indicated with arrows.

In addition, parameters for the Thomas-Fermi (TF) model can be set via:

```
fix_modify <ID> tf <type> <length> <volume>
```

with the parameters length and volume corresponding to the TF length, $l_{TF}$, and and the reciprocal particle density, $d^{-1}$, in Ref. 10, respectively. Parameters need to be specified for each atom type in the electrode. Further, the pppm/electrode long-range solver can be configured to calculate its part of the elastance matrix in two steps:

```
kspace_modify amat [onestep/twostep].
```

This twostep option can be faster for large electrodes and moderate mesh sizes but requires more memory11.

The particle charges of the relevant electrode groups will then be dynamically updated over time, resulting in a MD simulation with CPM, CCM or TP dynamics as selected. These electrode charges are accessible using standard LAMMPS commands.

**B. Implementation**

In contrast to previous versions, our implementation separates the class for charge updates from the computation of the elastance matrix and the electrolyte vector $b$. The FixElectrode class is
derived from the LAMMPS Fix class and is used to determine and set electrode charges. As shown in Fig. S1, the computation of the short-range, long-range and self interaction as well as the boundary correction are distributed across four additional classes.

The ElectrodeMatrix and ElectrodeVector classes handle the computation of the elasticity matrix and electrolyte vector, respectively, with each class containing its own code for the short range Coulombic interactions. For long range interactions and boundary corrections, the two classes in turn delegate computations to implementations of the abstract ElectrodeKSpace class. The two implementations inherit from the LAMMPS KSpace classes for the Ewald summation and particle-particle particle-mesh (P³M) method, respectively. For the functions of ElectrodeKSpace, additional Fourier transforms for the electrolyte charges and the Green’s function at the position of electrode particles have been implemented\textsuperscript{11}. A BoundaryCorrection class was also added, which encapsulates the existing LAMMPS implementation of the EW3DC method\textsuperscript{1,2} and adds new implementations for exact 2D Ewald summation\textsuperscript{12,13} and a “wire correction” method intended for 1D-periodic systems\textsuperscript{1,3}.

As developers, we have found our experience writing the ELECTRODE package to be a textbook example of the advantages of object-oriented programming done well. Splitting the code across distinct classes has significantly clarified information flows between the different parts of the ELECTRODE package, leading to easier maintenance and optimization.

\section*{III. SIMULATION DETAILS}

A capacitor with an aqueous NaCl electrolyte between two gold electrodes has been adapted from an example provided in the MetalWalls repository\textsuperscript{14}. For a consistent comparison, systems are equilibrated with the respective method at 0 V for the CPM and TP methods and at 0 e\textsuperscript{−} for the CCM methods. After an equilibration time of 5 ns, a total number of 100 equilibrated structures are written at an interval of 10 ps. For each of the resulting structures a charging process is modeled by applying a potential difference of 2 V or a roughly equivalent 4.4 e\textsuperscript{−}, depending on the method. The charging times $\tau$ are then obtained by fitting an exponential charging function $M_z^\text{eq} \left[1 - \exp(-t/\tau)\right]$ to the $z$-component of the electrolyte dipole for each of the 100 runs and taking the mean value.
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