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Porting of codes and atomic scale configurations



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1. Introduction

Computational materials modeling plays a crucial role in the design of devices for efficient low-cost energy generation and storage. The accuracy of predicted macroscopic quantities depends on which atomic-scale models are chosen and how they are implemented on large length and time scales. Despite the large demand of computer resources, materials modeling has a considerable impact in research and industry areas. For these reasons some key energy applications are used to develop a procedure to route the models toward HPC infrastructures and techniques. Inorganic and organic photovoltaics (PV), supercapacitors and batteries are applications where the knowledge of physical and chemical processes at the atomic-scale is recommended to better understand their macroscopic behavior.

The general main objectives of WP3 are:

- To provide a set of computational routines for morphology, electronic structure and transport properties of energy-related materials for PV, batteries and super-capacitors;
- To set up a methodology for designing materials for PV, rechargeable batteries and supercapacitors with optimal energy conversion and storage capabilities;
- To demonstrate how the computing infrastructure can address challenging problems in the field of energy by focusing on their atomic scale origin.

In this respect, deliverable D3.1 concerns both the activities described in task T3.1 (Section 2) and those, described in task T3.2, already started but not yet concluded, concerning the atomic scale description of the materials (Section 3).

Task 3.1 is devoted to the development of reliable atomic-scale models of materials to simulate key properties and chemical processes of interest in energy devices. ENEA, as reported in Subsection 2.1, has focused on the production of reliable atomic-scale structures of both amorphous silicon (a-Si) and hydrogenated amorphous silicon (a-Si:H). Their characterization via quantum molecular dynamics (MD) has been performed in order to build a reliable interface with a crystalline structure (c-Si). The interface of a-Si with a crystalline surface (a-Si:H/c-Si) has been also characterized. CEA, as described in Subsection 2.2, developed and ported methods via charge analysis to facilitate the parametrization of the force fields using Density Functional Theory (DFT). This will be applied to organic molecules and also to batteries (interaction between graphite-like electrode and electrolyte). UBAH and Maison de la Simulation (CEA, CNRS), as described in Subsections 2.3 and 2.4, used classical MD and DFT methods to address bulk and nanostructural properties of new perovskite materials for solar cells alongside electrode and solid electrolyte materials to enhance their energy density. This work is linked up with complementary MD and classical DFT studies on supercapacitor materials at CNRS.

2. Task T3.1: Atomic structure (from M1 to M24)

2.1 Development of an atomic structure of a-Si, a-Si:H and interface a-Si:H/c-Si (Celino)

The silicon hetero-junction (SHJ) technology holds the current efficiency record of 25.6% for silicon-based single junction solar cells and shows great potential to become a future industrial standard for high-efficiency crystalline silicon (c-Si) cells. The a-Si:H/c-Si interface, while central to the technology, is still not fully understood in terms of transport and recombination across this nanoscale region, especially concerning the role of the

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Figure 1: Hydrogenated amorphous Silicon 512 Si + 64 H thermalized at room temperature after annealing at T = 600 K. Silicon and hydrogen atoms are in yellow and blue, respectively.

different localized tail and defect states in the a-Si:H and at the a-Si:H/c-Si interface and of the band offsets and band bending induced by the heterostructure potential and the large doping, respectively.

Quench from the melt technique has been adopted to produce the atomic-scale model of amorphous hydrogenated silicon (a-Si:H) [1]. This is a standard method already successfully used and optimized on other similar systems [2, 3, 4, 5]. Several liquid configurations have been produced to disorder randomly generated starting configurations. Long enough simulations are used to lose memory of the starting atomic-scale features. Structural analysis and self-diffusion coefficients are used to characterize the liquid samples and to understand the role of the hydrogen. The content of hydrogen is about 11% that is the nominal concentration set in experimental materials optimized for PV performance [6]. The volume is chosen to be fixed to the experimental density value of 2.214 gr/cm³ [7]. Initially, a small system of 64 Si + 8 H atoms in a cubic supercell with size L = 11.06 Å, is considered, then, a big system (8 times greater) with 512 Si + 64 H atoms and L=22.12 Å is produced. The small system has been used to generate in parallel many different quenched configurations from which a subset has been chosen to model a greater atomic system. The greater atomic system has been then relaxed via annealing procedure (T = 600 K) to obtain a final room-temperature configuration. The reliability of the amorphous configurations have been checked against experimental results by combining structural (radial distribution functions, coordinations, average distances, chemical order) and electronic (eDOS, gap, electronic localizations, total energy) characterizations. From the radial distribution function it is possible to compute the coordination numbers and understand the nearest environment of every Si atom. It is interesting to note that the average coordination number of Si atoms is 3.99 because 99.0% of Si atoms have fourfold coordination, in agreement with experimental results. In particular 443 Si atoms have 4 Si atoms as nearest neighbors and 64 Si atoms have 3 Si atoms and 1 H atom as nearest neighbors. All the other types of coordinations are less that 1% (4 Si atoms have threefold coordination and 1 atom has five-fold coordination). It is valuable to find that neither isolated H atoms are present nor H_2 dimers, indeed all the 64 H atoms are bound to Si atoms. Moreover no atom is coordinated with two H atoms. In Fig. 1, the atomic-scale amorphous configuration thermalized at room temperature is shown.





Figure 2: Reconstructed (001) silicon surface p(2x1). The reconstructuted surface is used to built up the interface because it is significantly more stable than the ideal one.

Both crystalline bulk and crystalline surface configurations were generated and checked against experimental results. Moreover the crystalline surface was considered in its reconstructed configuration because more stable than the ideal one. A careful analysis of the void above the surface and of the number of planes under the surface was performed in order to avoid interactions between mirror images in z-direction. In Fig. 2, the unreconstructed (ideal) Si(001) surface is shown.

The interface shown in Fig. 3a), is used as starting configuration for Born-Oppenheimer molecular dynamics (BOMD) as implemented in the Quantum ESPRESSO (QE) suite [9, 10] and Quickstep code of the CP2K suite [11]. The ab-initio PWscf (Plane-Wave Self-Consistent Field) code of QE has been extensively used to model both the c-Si and the hydrogenated amorphous Silicon (a-Si:H). PWscf performs many different kinds of self-consistent calculations of electronic structure properties within DFT [12, 13], using a Plane-Wave (PW) basis set and Pseudo-Potentials (PP). On the contrary, CP2K has been mainly used to model the interface since it can scale-up with good performance on very large numbers of processors. All the calculations were performed in the supercell approximation with periodic boundary conditions (PBC) meant to mimic infinitely extended systems. Si and H ultrasoft pseudopotentials with Perdew-Burke-Ernzerhof (PBE) [14] approximant GGA exchange-correlation potential, available in the Quantum ESPRESSO library, were used [10]. The electronic wave functions were expanded in a plane-wave basis set with a kinetic energy cut-off equal to 40 Ry (the charge density cut-off was 240 Ry). Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-newton algorithm was used to perform geometry optimization. Ionic relaxation was stopped when both the following conditions were satisfied: energy changes less than 10^{-4} Ry between two consecutive self consistent field (SCF) steps and all components of all forces were smaller than 5×10^{-4} Ry/Bohr. Simulations on the electronic ground state at constant volume and constant temperature (NVT ensemble), with timestep $t_s = 20$ Rydberg atomic units (~ 0.9676 fs) and saving the configurations at every timestep, have been performed. Ionic temperature is fixed at T=





Figure 3: Crystalline-amorphous interface. a) snapshot of the starting configuration built up by putting the reconstructed surface and the amorphous system at the distance where the minimum of energy is attained. b) the interface after 25 ps of simulation at 600 K. c) thermalized configuration at room temperature after 35 ps.

300 K and is controlled using Andersen thermostat [15].

The first four layers of c-Si atoms on the left are kept fixed to impose a bulk like behavior to the crystalline silicon part of the interface system (Fig. 3). The MD simulation is performed for more than 35 ps, the first 25 ps of the simulation were used to thermalize the system and reach a stable configuration. The last 10 ps of the simulation (from 25 ps to 35 ps) were used to analyze the system. In panels b) and c) of Fig. 3, are shown the snapshots of the c-Si/a-Si:H interface at 25 ps and 35 ps, respectively. To characterize the interface we considered distinct groups of Si atoms at different distances from the interface and we used them to evaluate the partial radial distribution functions and their coordinations. Moreover the interface was characterized by considering couples of Si atoms formed by one silicon atom on the c-Si surface and one a-Si atom at distance lower than typical nearest-neighbor amorphous distances. This approach enlights that the interface is very chemically ordered and confirm our approach. This is an important step because this model can be now used to generate selected types of defects and to characterize them respect to the ideal reference configuration. Moreover this ideal configuration can be repeated in the plane x and y to generate larger configurations to be run on more powerful computers.

Both CP2K and PWscf codes have been used on HPC infrastructure available to the project, ENEA and JUELICH supercomputers. PWscf benchmarck has been performed in order to compare the systems and understand the materials models requirements in terms

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Figure 4: Visualization of a DNA fragment containing 11 base pairs, surrounded by a solvent of water and Na ions (giving in total 15,613 atoms), with periodic boundary conditions.

of memory and speedup. Moreover the CP2K codes has been one of the codes evaluated during the second performance evaluation session in Saclay (France).

2.2 Development and porting of methods for force-field parametrization (Deutsch)

Development and porting of methods via charge analysis to facilitate the parametrization of the force fields using DFT. This will be applied to organic ions and also to batteries (interaction between graphite-like electrode and the electrolyte).

The linear scaling version of BigDFT builds an optimized localized atom-centered basis set for each atom expressed on Daubechies wavelets basis sets. Then the Hamiltonian, the overlap matrix and the density matrix can be expressed in this optimized localized basis set, and are sparse reducing considerably the cost of calculations. We can, actually, use this minimal basis set to express other quantities and doing, for instance, a charge analysis which is the natural way to compare with polarizable force fields. Charge analysis is the key quantity to perform QM/QM or QM/MM calculations using a polarizable force field.

First, the QM/MM approach is useful to calculate, for a given subsystem, quantities which are intrinsically only possible with an ab-initio approach, but influenced by a surrounding which does not require a strict first principles treatment. The calculation of the partial density of states is an example intrinsically requiring a QM treatment, which we will demonstrate for the system depicted in Fig. 4, showing a small fragment of DNA in a water-Na solution consisting in total of 15,613 atoms. The determination of the electronic structure is only possible using a QM method, but the influence of the environment on the DNA can also be modeled with a less expensive classical approach. In Fig. 5, we compare the outcome of a full QM calculation with a static QM/MM approach, where all the solvent except for a small shell around the DNA has been replaced by a multipole expansion





Figure 5: Partial density of states for the DNA within the system depicted in Fig. 4. The red curve was generated treating the entire system on a QM level, whereas the green curve only treated the DNA plus a shell of Å on a QM level, with the remaining solvent atoms replaced by a multipole expansion. In order to allow for a better comparison, the QM/MM curve was shifted such that its HOMO energy coincides with the one of the full QM approach.

up to quadrupoles, leaving in total only 1877 atoms in the QM region. As can be seen from the plot, the two curves are virtually identical, but the QM/MM approach had to treat about 8 times fewer atoms on a QM level and was thus computationally considerably cheaper.

We show another example where large scale QM simulations are important to validate some QM/MM approaches. Sometimes one is interested in atomistic characteristics averaged over a large number of samples, in this way generating the macroscopic behavior. An example is the dipole moment of liquid water, which is a macroscopic observable with a microscopic origin. In order to calculate it accurately it is not sufficient to simply compute the dipole moment of one water molecule in vacuum. Instead one has to take into account the polarization effects generated by the other surrounding water molecules. Due to thermal fluctuations each molecule will however yield a different value, and the macroscopic observable result (keeping in mind that this can only be determined indirectly and is thus itself subject to fluctuations) can therefore only be obtained by averaging over all molecules, thereby requiring a truly large scale first principles simulation. The outcome of such a simulation, carried out using the MM code POLARIS(MD) and the QM code BIGDFT is shown in Fig. 6. Here we plot the dispersion of the molecular dipole moments, calculated based on atomic monopoles (i.e. atomic charges and dipoles) of a water droplet consisting of 600 molecules at ambient conditions and taking 50 snapshots of an MD simulation. As can be seen, there is a wide dispersion of the molecular dipole moments, which however yield a mean value in line with other theoretical and experimental studies.

We improved considerably the linear scaling version of BigDFT, mainly working on the parallelization. In September 2016, our record is 250,000 atoms without loss of accuracy comparing to the cubic scaling version. We are working on improving the parallelization of hybrid function calculations.

In collaboration with Basel University, we ported BigDFT on GPU architecture with the new scheme GPUdirect. We applied to a Gordon Bell award for that. We are currently testing new architectures thanks to the BOAST technology developed in collaboration with LIG (Laboratoire Informatique de Grenoble) as OpenPower and Xeon Phi.





Figure 6: Dispersion of the molecular dipole moment of water molecules within a droplet of 1800 atoms, with statistics taken over 50 snapshots of an MD simulation. The dipole is calculated based on the atomic monopoles and dipoles, and these were obtained from a) a classical simulation using POLARIS(MD), b) a DFT simulation using BIGDFT, and c) a combined QM/MM approach.

2.3 Metadynamics (Walker)

UBAH and Maison de la Simulation (CEA, CNRS), as described in Subsections 2.3 and 2.4, used classical MD and DFT methods to address bulk and nanostructural properties of new perovskite materials for solar cells alongside electrode and solid electrolyte materials to enhance their energy density. This work is linked up with complementary MD and classical DFT studies on supercapacitor materials at CNRS.

Perovskite cells suffer from hysteresis due to the motion of iodide vacancies. Existing molecular dynamics codes have difficulty in isolating this motion from that of the non-mobile ions. Metadynamics is being investigated as a way of addressing this problem. Bath has shown hysteresis arises due to the motion of iodide vacancies. Figure 7 is taken from the paper by the group of S. Islam [16].

An example is given in Figure 8 obtained by Walker and her group (unpublished) that demonstrates how time evolution of currents for an unilluminated cell after a bias is applied is affected by vacancy motion. This result was obtained by a continuum (drift diffusion) model. Task 3.1.3 is developing a multiscale model that links microscopic calculations of ion vacancies to the macroscopic drift diffusion model that produced Figure 8.

Existing molecular dynamics codes have difficulty in isolating the motion of defects in the perovskite layer from that of the non-mobile ions. Metadynamics is being investigated as a way of addressing this problem. This technique, reviewed in A. Laio and F. Gervasio [18], accelerates rare events. In our case, these rare events are iodide vacancy motion between two lattice unit cells.

A Kinetic Monte Carlo, KMC, simulation code for perovskite cells is being developed as a mesoscopic simulation of charge transport. In this way, we can bridge the length scales between the atomistic molecular dynamics simulations and our drift diffusion code. We will adapt the work of Kerisit and Rosso [19] who use KMC to study charge transport in





Figure 7: Left panel: Evolution of conduction band profile due to ion motion Right panel: resulting evolution of dark current for different applied potentials once bias is switched on.



Figure 8: Top panel: vacancy trajectory. Bottom panel: energy variation across this trajectory.





Figure 9: Schematic of the polyhedral ring topologies in (a) cubic and (b) tetragonal LLZO. Triangles represent tetrahedra, and rectangles represent octahedra. Arrows indicate neighbouring octahedra within conjoined rings. The lithium sites shown are those identified by X-ray analysis by Awaka et al. [20]. In c-LLZO lithium resides at off-center positions in the octahedra, and is disordered over all available octahedra and tetrahedra. In t-LLZO lithium is ordered over two tetrahedra and four octahedra in each ring. White circles show these lithium sites, which are partially occupied in c-LLZO. The variation in polyhedral colours in t-LLZO shows the inequivalent sites due to the reduced crystal symmetry relative to c-LLZO.

haematite (α -Fe₂O₃).

2.4 Atomic structures for batteries and supercapacitors (Salanne)

Batteries and supercapacitors play complementary roles in the field of energy storage. While the former are characterized by large energy densities, which makes them suitable for many applications such as in electric vehicles, supercapacitors show better power densities and are therefore used when fast charges/discharges are needed. Both devices would highly benefit for a better understanding of the atomic structure of the solid materials and of the liquid electrolytes which are involved. In this project, we focus on the family of LLZO solid electrolytes for Li-ion batteries and on the study of nanoporous carbon-based electrodes for supercapacitors.

Methods and scientific results: Li-ion batteries

Conventional lithium-ion batteries rely on unstable liquid-organic polymer electrolytes, which pose practical limitations in terms of flammability, miniaturization, and safe disposal. A possible solution is to replace liquid electrolytes with inorganic ceramics that are electrochemically stable and non-flammable. The family of garnet-like oxides with general formula $\text{Li}_x M_3 M'_2 O_{12}$, where M = La and M' = Nb, Ta or Zr, have attracted significant attention in this regard due to their high lithium-ion conductivity, high electrochemical stability window, and chemical stability with respect to metallic lithium [21]. The highly stuffed garnet $\text{Li}_7 \text{La}_3 \text{Zr}_2 O_{12}$ (LLZO) is the most studied member of this family, and can be considered prototypical. LLZO exhibits two phases with strikingly different ionic conductivities: a cubic phase (c-LLZO) that is adopted at high temperature (>600 K) or stabilized by doping [22] with $\sigma \approx 10^{-4} \text{ S cm}^{-1}$, and a tetragonal (t-LLZO) phase with $\sigma \approx 10^{-6} \text{ S cm}^{-1}$ that is favoured in the pure system at ambient temperature. The different topologies of the two phases are illustrated on Figure 9.

In order to study the structure of these systems, we have performed molecular dynamics simulations of various garnets using the Metalwalls code. A $2 \times 2 \times 2$ supercell con-

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Figure 10: (a) Calculated lattice parameters (Å) for LLZO as a function of temperature (K). The *a* parameter is shown in blue, the *b* parameter is shown in magenta and the *c* parameter is shown in orange. Literature values from Adams and Prasada Rao for XRD and MD [23], as well as, Rangasamy *et al.* [24] and Larraz *et al.* [25]. (b) Calculated lattice parameters (Å) at 300 K as a function of Li vacancy (V_{Li}) concentration, *z* for Al–LLZO (top), Nb–LLZO (middle) and Ta–LLZO (bottom). The *a* parameter is shown in blue, the *b* parameter is shown in magenta and the *c* parameter is shown in orange.

taining 1536 atoms was used for pure LLZO, and the number of atoms was modified to give the corresponding compositions for the doped structures. A timestep of 1 fs was used for all simulations. The system was equilibrated for temperatures ranging between 300 K and 1000 K in the isothermal-isobaric (NPT) ensemble. The supercells were initially equilibrated at a temperature of 280 K for 10 ps; the temperature was then scaled up to 1000 K at a rate of 1 K ps⁻¹. Production runs were performed in the canonical (NVT) ensemble using the equilibrium values from the NPT simulations and were up to 87.4 ns long.

The room temperature lattice parameters from the simulations are approximately 1% larger than experimental values, which is consistent with the DFT calculations used to parameterize the force fields. By monitoring the evolution of the lattice parameters with temperature as shown on Figure 10(a), it is possible to determine the temperature of the transition from t-LLZO to c-LLZO. A value of 620 K is obtained in the simulations, in good agreement with the experimental data. Then the amount of dopants that need to be added for stabilizing the cubic phase at 300 K was determined for Al, Nb and Ta, as shown on Figure 10(b). It is then possible to determine the ionic conductivity with respect to the temperature and the compositions, in order to determine which conditions would enable the use of LLZO as electrolytes in solid-state Li-ion batteries. These results will be discussed in a further deliverable.

Methods and scientific results: supercapacitors

Nanoporous graphene-based electrodes

The optimization of carbon-based supercapacitors is of fundamental importance for electrical energy storage. In order to achieve supercapacitors high-performance, it is necessary to understand the molecular mechanism of adsorption of ions inside the pores of the carbon electrodes. With the purpose of overcoming the limits of classical graphene and obtaining increased energy per unit of volume, we analyzed systems consisting of perforated graphene (Figure 11), which allows the diffusion of the ions between the sheets and

Figure 11: Simulation cell of a BMIM-PF₆ ionic liquid surrounded by nanoporous graphene electrodes. Color scheme; blue: 3-site BMIM⁺ molecules, red: single-site PF_6^- molecules, green: carbon electrode atoms.

provides us with fast charging and discharging rates, and an ionic liquid electrolyte.

We performed classical molecular dynamics simulations with the Metalwalls code. The two main characteristics of these simulations consist, on one hand, in the possibility of maintaining the electrodes (each one composed of 10627 carbon atoms distributed among 6 perforated graphene planes) at constant potential by allowing the charge of the carbons of the electrode (represented by Gaussian distributions centered on the atom) to fluctuate at each time step, which is essential to obtain a realistic behavior of the ionic liquid/electrode interface[26, 27]. On the other hand, the simulations were carried out by using a non-polarizable coarse-grained model to mimic the behavior of the chosen ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) [28].

In order to analyze the structure of the ionic liquid adsorbed within the electrodes, we studied the number density profiles as a function of the spacing between adjacent planes of graphene (from 7 Å to 10 Å). In Figure 12 we can observe the molecular reorganization induced by the charged electrodes, which is reflected in the formation of high density peaks on the inside and in the vicinity. The local density of anions in the positive electrode is higher than that of cations in the negatively charged one, as expected from their smaller size that allows for accommodating more negative ions in the layers. In addition, the height of the peaks is greater in the more confined system (d=7 Å), which is due to the partial desolvation of the ions when they are confined in pores whose size is in the same range as the ion size. This is an evidence of the influence of the pore size on the performance of supercapacitors and the importance of selecting an electrode/electrolyte couple that leads to an efficient ion adsorption. In the system with an interlayer spacing of 10 Å it can be also seen the formation of a double peak that shows that the ions can place themselves at

Figure 12: Number density profiles in the proximity of the positive electrode for the BMIM⁺ (red lines) and PF_6^- (green lines) ions, in the direction perpendicular to the electrodes, for a distance between consecutive planes of 7 Å and a potential difference of 1.8V (left) and for a spacing between graphene planes of 10 Å and a potential difference of 1.0V (right), both at 400 K.

two different distances between two consecutive planes of graphene. In further deliverables the impact of these structural changes on the capacitance will be discussed.

Effect of the electrolyte composition in carbide-derived carbon electrodes

Table 1:	Electrolyte	$\operatorname{compositions}$
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ACN mass %	0 (pure ionic liquid)	10	20	40	67
Ion conc. (mol/L at 298.15 K)	6.40	5.28	4.58	3.01	1.51
$EMIMBF_4$ Ion pairs	600	601	608	326	324
ACN molecules	0	322	733	1048	3172

The choice of the liquid will also impact strongly the performance of supercapacitors. Therefore, a second series of simulations was performed where we systematically varied the electrolytes compositions. We simulated mixtures of acetonitrile (ACN) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) with various concentrations, as summarized in 1. Coarse-grained models for ACN and EMIMBF₄ were obtained from Edwards *et al.* [29] and Merlet *et al.* [30] respectively. The simulation boxes consist of EMIMBF₄ and ACN surrounded by two symmetric carbide-derived carbon electrodes, with an average pore size of approximately 0.75 nm, as shown on Figure 11. The model electrodes were obtained by molecular dynamics from Palmer *et al.* [31] by quenching a sample of liquid carbon consisting of approximately 4000 atoms with a rate of 20×10^{12} K s⁻¹. Finally the carbon Lennard–Jones parameters of $\sigma = 0.337$ nm and $\epsilon = 0.23$ kJ mol⁻¹ were obtained from Cole *et al.* [32].

Figure 13: Simulation cell of an EMIM-BF₄ and ACN electrolyte mixture surrounded by disordered porous Ti-CDC800 electrodes. Color scheme; blue: 3-site EMIM⁺ molecules, red: single-site BF_4^- molecules, pale yellow: 3-site ACN molecules, silver: carbon electrode atoms. Gray molecules cap the cell in the z-dimension, as this is non-periodic.

Initial equilibration and pore filling was performed in open source MD package GRO-MACS [33]. Firstly, the liquid electrolytes were equilibrated at 340 K. The liquid boxes were then placed between the electrodes and allowed to relax in the NVT ensemble. Pore filling rate was enhanced by cycling the constant charge values of the electrode atoms between ± 0.01 e for 10 iterations. The boxes were then equilibrated at zero electrode charge for 500 ps. Second stage equilibration was performed with Metalwalls. The distance between the electrodes was tuned by position rescaling for each system, such that the bulk densities matched those of the pure EMIMBF₄/ACN mixtures at 1 bar and 340 K. The temperature of 340 K was chosen to increase the ion mobility and reduce the required simulation time. Once correct bulk densities were achieved, the final equilibration step was performed with velocity rescaling and electrode atoms charged to constant values of ± 0.01 e for the positive and negative electrode, this step was run for several nanoseconds so that sufficient equilibrium was achieved.

For production runs, the electrodes were switched to a constant potential and the systems were run in the NVE ensemble with ± 0.5 V for the half cell potentials of the positive and negative electrodes. The length of production runs exceeded 12 ns to ensure that average electrode atom charges had reached a steady equilibrium value. 2D Ewald summation [34, 35] was used for all Coulombic interaction calculations, with a short range cut-off distance of 22 Å (half the length of the x and y cell dimensions). Lorentz-Berthelot combination mixing rules were employed for non-bonded potential interactions.

The main results from the MD simulations is to provide the electrolyte compositions inside the pores as a function of ACN concentration, which are shown. These are shown in Figure 14 for uncharged electrodes and for an applied voltage of 1 V between them. A large linear variation is observed in all cases, ruling out the existence of a saturated regime. Over the whole composition range, there are consistently more ions in the positive electrode at 1 V, which is most likely an ion-size effect. For the pure EMIMBF₄ system, in the positive electrode it is more favorable to remove a small amount of large EMIM co-ion and insert a greater amount of small BF_4^- counter-ions. In the negative electrode the opposite was observed where are a greater amount of co-ions were expelled, and a smaller amount of cations were inserted. At 20% mass fraction ACN, it appears that some co-ions were trapped inside the negative electrode, possibly in pores with no clear path to exit. This has caused a greater than expected number of counter-ions to be inserted to induce charge in the electrode. We observe that the difference between the number of counter- and co-ions, hence the net charge (dashed green line), is almost constant at 1 V, which results in similar total induced charge in each electrode despite the large variation

Figure 14: Electrolyte composition inside the electrodes. Light green: uncharged CDC electrodes; Orange/Blue: electrodes held at a constant potential difference of 1 V. Dark green: difference between the counter-ions and the co-ions numbers for the 1 V simulation.

in the total number of ions. This means that the performance of the devices should not be much affected by the electrolyte concentration, a point which will be addressed in a further deliverable of the project.

3. Task T3.2: Ab-initio electronic and photonic structure (from M6 to M30)

Based on the atomic structures inherited from Task 3.1, the present Task 3.2 aims to develop efficient real-space embedded density functional theory and many-body perturbation theories (MBPT= GW, Bethe-Salpeter) for accurate ab-initio descriptions of the electronic and optical properties of the active part of organic and hybrid systems (interfaces, defects, dopants, etc.) while fully accounting for the effect of the environment (solvent, dielectric, electrodes, etc.). The real-space formulation allows a description of electron and exciton hopping energies to feed the mesoscale analysis as described in task T3.4 in connection with the applications described in T3.5.

In this deliverable, the main results of the activities concerned with the atomic-scale description of the materials are only reported. In the next Deliverables the full description of Task T3.2 will be reported.

3.1 Methods to characterize oPV (Duchemin)

A validation scheme devoted to providing reference electronic properties data on few hundred atom systems (e.g. a dopant with its first shell of neighbors) has been set-up, combining state-of-the-art many-body perturbation theory for finite size systems (the GW and Bethe-Salpeter formalisms, as implemented in the FIESTA package), with an accurate micro-electrostatic approach (the MESCAL package) allowing to account for the electrostatic and polarization effects generated by the environment. The goal is to validate, with one of the most accurate methodology for systems of that size, the larger scale approaches (constrained-DFT, microelectrostatic techniques, etc.) that will be used in production modes on the atomic structures inherited from Task 3.1.

Figure 15: Embedded HOMO calculated for a F4TCNQ dopant within Pentacene crystal. The six pentacene first neighbors are treated explicitly, while the rest of the molecular crystal influence is described through discrete polarizable model techniques.

The merging of the GW and microelectrostatic techniques requires to know the response (reaction field) of the polarizable medium to various charge distributions in the QM region as described by an auxiliary basis, namely a collection of atom-centered s, p, and dlike charges (higher angular momentum are useless). These calculations (parallelized over the auxiliary orbital basis) are used to construct the reaction field matrix in the auxiliary basis that allows computing the polarization energy to any charge distribution, namely any charged electronic level or multipolar perturbation, in the QM region. The cost of the reaction-field matrix constructed with MESCAL grows linearly with the QM system size (namely with the size of the auxiliary basis), while the cost of the GW calculations grows as its fourth-power. The required inputs are the atomic coordinates (and atomic number) of the active QM cluster together with the atomic coordinates and polarizabilities of the surrounding MM environment under the form of a large cluster surrounding the QM partition. A black-box calculation with default parameters (e.g. cc-pVTZ Dunning basis with Weigend Coulomb fitting auxiliary basis) is possible, starting with DFT calculations for the QM cluster (isolated) performed by the open-source NWChem code that automatically provides the necessary input for the GW and Bethe-Salpeter calculations. A typical GW/ME calculation (cc-pVTZ level) on the pentacene/F4TCNQ/pentacene taken from the cluster shown as an Inset (Figure 15) amounts to 2 hours wall-time on 96 cores of a standard laboratory cluster.

In practice, the GW and Bethe-Salpeter (BSE) formalisms provide the entire spectrum of charged and neutral excitations as the solution of effective eigenvalue problems involving the screened Coulomb potential W that accounts for polarization effects. The environment microelectrostatic (ME) contribution to the screened Coulomb potential W allows incorporating the reaction of the surrounding classical (MM) polarizable medium to an excitation in the (QM) subsystem treated at the GW/BSE level. Once the environment contribution to W is incorporated, the GW/BSE calculations can proceed as in a standard gas phase calculation. We demonstrated that our scheme fully accounts for polarization effects from both the QM and MM subsystems, while fully accounting to

Figure 16: Convergence of the self-consistent electronic structure of an a-Si:H/c-Si interface configuration (368 atoms) w.r.t. cut-off energy and number of k-points.

all charge-transfer and hybridization effects in the QM subsystem of interest. In particular, as first applications, the bulk and surface electronic properties of pentacene could be accurately reproduced, and the strong hybridization scenario proposed by Koch and coworkers [17] for F4TCNQ-doped pentacene could be validated.

3.2 Methods for electronic structure characterization at the a-Si:H/c-Si interface (Aeberhard)

The atomic structure of the a-Si:H/c-Si interface as computed in T3.1.1 was used to determine the electronic states of the structure via the DFT code QuantumESPRESSO. Special consideration was given to the analysis of localized states in the vicinity of the interface, which can act as recombination centers.

Methods and scientific results

Electronic structure calculations. Self consistent density functional theory (DFT) calculations using Quantum ESPRESSO were performed for the interface configuration with 368 atoms to obtain the potential and charge density. The convergence for the interface is shown in Fig. 16. In a second step, the electronic structure, i.e., the electron wave functions and energies, were obtained in a non-selfconsistent calculation for different k-point grids $(N_{\text{kpoints}} = [1..512])$ as starting point for calculations of structural and electronic properties.

Calculation of (local) density of states and wave function localization. The electronic structure was post-processed to obtain information about the localization of the electronic states, and their distribution in energy space, which is important to identify localized states serving as recombination centers and distinguish them from extended states. To this end, the total and layer-resolved (local) density of states (DOS) was calculated (Fig. 17 top) as well as the spread (S) of the wave functions as a function of energy (Fig. 17 bottom).

Calculation of electron localization function. From the electronic wave functions the electron localization function (ELF) between the atoms was calculated using Quantum ESPRESSO to obtain information about the bonding in bulk a-Si:H and at the interface with c-Si. The ELF is first computed on a 3D grid, and then interpolated on the paths between neighboring atoms (Fig. 18). This allows the identification of atomic bonds and thus the calculation of the coordination number for each atom.

Figure 17: (Top) Local DOS integrated over layers parallel to the interface as a function of the z-coordinate. (Bottom) Wave function spread in z-direction. Each dot marks the energy and the position of the center of one wave function, where the color represents its spread. The dotted line shows the approximate position of the interface.

Figure 18: (left) 3-fold bond atom at the a-Si:H/c-Si interface. (right) The ELF between the atom and its nearest neighbors allows the identification of two silicon bonds, one hydrogen bond, and one broken bond.

Routines/Codes to design and characterize

All the results were obtained either from the direct output of QE (\rightarrow LDOS) or using customized post-processing routines (\rightarrow spread, ELF).

Porting on platforms

The QE computations were all run on JURECA.

3.3 Methods for supercapacitor characterization, code interfacing (Borgis)

Code evaluation and porting on platforms

MDFT code has been evaluated during the second performance evaluation session at MDLS, Saclay (France). Characteristic and target test cases have been defined and all HPC metrics (for instance memory consumption, CPU time, parallel performance) have been extracted with the help of an HPC expert, Matthieu Haefele (EoCoE WP1). The tool from Juelich, JUBE, is now in place for MDFT to automate the extraction of these metrics for forthcoming developments. Profiling on a production site, on Julich Supercomputers, especially JURECA, made it clear that MDFT should be less memory-intensive to fit on a single node. We thus improved the memory requirements in MDFT by a factor of 5 following the strategy recommended by the HPC experts of EoCoE:

- (i) moving from double to single precision, which is a big move that required special attention, and
- (ii) recalculating some of the biggest arrays like the external potential at each minimization cycle instead of storing them. An EoCoE Application report with great details on these aspects has been written.

Scientific results

Thanks to the code developments described above in EoCoE, MDFT is now able to tackle the large dimensions of the supercapacitors model used by METALWALLS: The external potential corresponding to the constant charge electrodes of Metalwalls is now implemented in MDFT. For the MDFT theory, the sole input to fully characterize the solvent is the spatial and angular dependent direct correlation function of the bulk, homogeneous, solvent. We produced this direct correlation function for the important case of acetonitrile from precise all-atom simulations. The most recent advances of MDFT were dedicated to water. After working on a generalization of the theory to arbitrary solvents, MDFT is now theoretically able to tackle solvation in acetonitrile.

3.4 Computation of light absorption (Aeberhard)

The main goal of this task is the development of a massively parallel FEM Maxwell solver for application in thin film PV. In a first stage, INRIA will test its code on data and structures provided by JUELICH. If this is successful, demanding light trapping architectures in silicon heterojunction solar cells will be investigated on the JUELICH supercomputers.

Figure 19: Generation of computational meshes for thin-film silicon solar cells.

Methods and scientific results

At the current stage, the activity in this task was focused on the efficient generation of computational meshes at INRIA for experimental topography and compositional data for thin-film silicon solar cells as provided by JUELICH (Fig. 19).

Routines/Codes to design and characterize

The Maxwell-solver under development by INRIA is based on a high-order discontinuous Galerkin time-domain method (details in corresponding WP1 task by S. Lanteri). The meshing as an important component of the numerical approach is largely based on the Gmsh tool.

Porting on platforms

Currently running on the local clusters at INRIA, porting to JURECA planned at a later stage.

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