# MaX

Materials Design at the Exascale

ANNEX II

## Pilot Case 1. Computational protocol for friction and tribochemistry (Key person: M.C. Righi, CNR, in collaboration with Total SAS and Toyota Europe)

### A protocol to calculate the interfacial shear strength from first principles

We defined a computational protocol to calculate from first principles the ideal shear strength, $\tau$, of solid interfaces. $\tau$ is a friction force per unit area and represents the maximum resistance to sliding of an interface. The possibility of evaluating this intrinsic interfacial property by calculations offers a very convenient way to predict the effects of the surface chemical modifications on tribological properties. This is important for example to design lubricant additives or low-friction coatings.
Despite the great interest of industries in developing new, environmental friendly lubricant additives, very little is known on the microscopic mechanisms that govern their functionality. It is known that boundary lubricants react with the metal surfaces, modify their chemical composition with consequent modification of their adhesion and friction properties.

The protocol we developed consists in the following steps:

1) Calculating the work of separation, $W_{sep}$, which represents the energy per unit area required to separate two surfaces from contact, as $W_{sep} = (E_{interf} - E_{surf1} - E_{surf2})/A$, where $E_{interf}$ is the total energy of the system containing the two surfaces in contact, $E_{surf1,2}$ is the energy of the isolated surfaces, A is the surface area. In the present work we consider interfaces composed of identical surfaces, therefore $E_{surf1} = E_{surf2}$.

2) Constructing the potential energy surface (PES) of the sliding interface.
The work of separation is a function of the relative lateral position of the two surfaces in contact. This energy variation can be described as a potential energy surface (PES) with minima and maxima. The minima correspond to the relative positions where the two surfaces adhere in the optimal way, for example, by establishing chemical bonds across the interface. The maxima of the PES correspond to relative positions where these bonds are stretched or eventually broken. Therefore to displace one surface with respect to the other, the energy to climb the PES maxima (or PES saddle points) should be provided to the system. The energy difference between the maxima and the minima is usually referred to as the PES corrugation. It corresponds to

the maximum amount of energy that can be dissipated by frictional mechanisms, such as the excitation of phonons or the activation of chemical reactions that can modify the surface structure and composition.
The PES is constructed by calculating the $W_{sep}$ for several relative lateral positions, typically of high symmetry, and then interpolating. The calculations can be performed both at zero and under uniaxial stress (load).

3) Calculating the frictional forces that arise when the slider is displaced along symmetry directions by mathematical derivation of the PES profiles along that directions. Typically we consider the minimum energy path as it posses has the highest statistical weigth. It connects the PES minima passing thorough the PES saddle points.

4) We define the ideal interfacial shear as the highest resistance force, f, along each considered path, normalized by the contact area: $\tau = f/A$. The calculated values should be regarded as limiting values because the simulated surfaces are infinitely flat. Nevertheless, comparison of the different interfaces can provide useful information to understand the effects of the surface termination observed experimentally.

In the following is described an example of application of the above procedure. The results allowed us to identify the different effects of sulfur and phosphorus, which are key elements for high-pressure additives, in reducing the shear strength of iron.
A bidimensional representation of the PESes obtained for S and P-passivated sliding interfaces is shown in Fig. 1a, a common energy scale is used, where the minima are colored in blue. The ball-and-stick inset offers a top view representation of the substrate surface. An identical surface shoud be imagined sliding on it. The labeled white dots indicate the relative positions considered in the calculation of the PES. The PES corrugation of the P-passivated interfaces is much higher than that of the S-passivated ones, consistently with the higher adhesion calculated for the P-passivated interface. It is noticed that in spite of a more pronounced load-induced increase, the energy barriers that should be overcame to slide S-passivated surfaces are lower than those of P-passivated surfaces. This produces lower frictional forces.

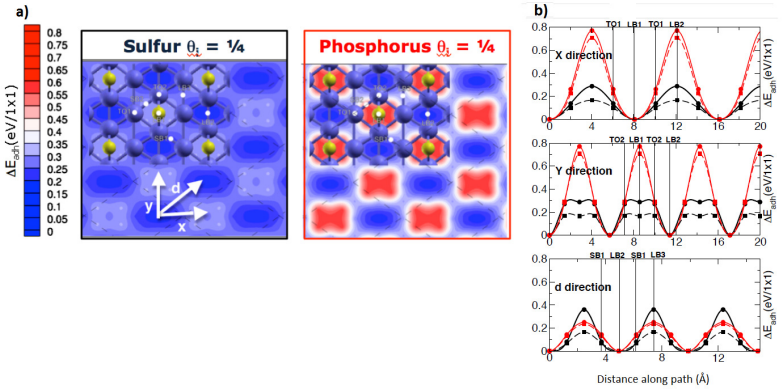

Figure 1: panel a) Bidimensional representation of the PES obtained for S- and P-passivated interfaces at zero load, panel b) PES profiles along the three symmetry directions indicated with arrows in Fig. 1a. The red (black) color is used for the P-(S-)passivated interfaces, a continuous (dashed) line is used for 10 GPa (zero) applied load.

If we consider the "d" direction, which corresponds to the minimum energy path that connects the PES minima passing through the saddle points, we can notice that the resistance to sliding of a clean iron interface at zero applied pressure is of 4 GPa. A 60% reduction is obtained by including interfacial phosphorus in a small concentration of 0.25 ML. This reduction reaches the 70% if sulfur is used instead of phosphorus (third line of Tab. 3).

Table 1: Ideal shear strengths along high symmetry directions for clean and passivated interfaces

| | Clean interface | P coverage ¼ ML | S coverage ¼ ML |
|---|---|---|---|
| $\tau_x$ (GPa) | 32.5 | 8.9 | 1.9 |
| $\tau_y$ (GPa) | 46.0 | 11.0 | 2.5 |
| $\tau_d$ (GPa) | 10.2 | 4.1 | 3.0 |

The surface passivation decreases the Fe-Fe interaction at the interface, decreasing friction and adhesion, especially at high coverage. Our calculations reveal that P and S are good passivating species, as they create electrostatic and Pauli repulsion at short distances.
The above predictions have been confirmed by gas phase lubrication experiments, where friction experiments as well as *in situ* surface analysis have been performed. [M.C. Righi, S. Loehlé, M.I. De Barros Bouchet , S. Mambingo-Doumbe and J. M. Martin, accepted for pubblication in RSC advances].

The development planned for the next months is to automatize the protocol for the first principle calculation of the ideal shear strength by means of the Aiida plarform. The above described procedure is, in fact, constituted of a clearly defined flowchart, where at some steps, such as the PES construction, many calculations should be repeated several time.

## Pilot Case 2. Computational protocol for understanding thermal energy storage in molten salts and nanofluids (Key person: P. Ordejon, ICN2, in collaboration with Abengoa Research)

**Industrial Interest**

Innovation is a key factor for realising the potential of novel, renewable and clean energy sources to compete with fossil fuels. Improving the efficiencies and thus lowering the cost of energy generation is essential for the economic viability of novel, renewable and clean energy sources. Solar thermal energy is one of the most competitive alternatives: the heat generated can be stored in a heat storage medium by means of an intermediate heat transfer fluid, for further transportation and use.

Molten salts are one of the preferred options used by industry. Optimising the thermal storage and transport properties of molten salts is therefore key for the global efficiency of these technologies. One of the options for improving these properties, in particular thermal conductivity and specific heat, is to introduce nanoparticles dispersed in the molten salt. Simulation plays a very important role in this research and innovation process, as producing reliable experimental data for these systems is difficult and expensive. Within MAX, we will collaborate with Abengoa Research to elaborate computational protocols for the determination of the key thermal parameters of molten salts containing nanoparticles. The protocols will then be made public, and will be tested and used by Abengoa Research, within their proprietary activities.

**Target**

Within MAX, we aim to elaborate computational protocols for the determination of the key thermal parameters of thermal storage fluids like molten salts, and to predict and explain the modification of these properties by the addition of nanoparticles (the so-called nanofluids).

**The protocol**

We are setting up a protocol for the study of two specific thermal properties of molten salts and nanofluids: the heat capacity and the thermal conductance. In a first stage, we are establishing and testing this protocol on the basis of classical Molecular Dynamics (MD) simulations, using classical force fields, but the protocols should be general enough to allow a direct transition to the use of ab-initio MD codes. The steps of the current protocol are:

The choice of an appropriate interaction potential to describe the specific fluid under study. Both AMBER and the OPLS-AA force fields have been used for our test cases in classical MD runs, using LAMMPS.

Setting-up of the simulations. Antechamber and leap packages in Amber are used in order to set up the topology files and the force field parameters for both solutes and solvents

System preparation and equilibration: The setup of our system consists of two parts: the equilibration and production MD. The equilibration part involves 3 steps: a) short simulation in NVE ensemble, at low temperature (~10K), b) short simulation in NVE at room temperature (~300 K) and c) short simulation in NPT ensemble at room temperature (~300 K) to ensure the correct density of the systems involved.

Production runs: The production run involves MD in NPT ensemble at temperatures of interest. From the production runs we evaluated the heat capacity, the diffusion coefficient and the thermal conductivity of the systems.

Calculation of the isobaric heat capacity, $C_p=(\delta<H>/\delta T)_P$ where <H> is the ensemble average enthalpy readily available from a simulation from the slope of the enthalpy-temperature curve at four different temperatures.

Calculation of the self-diffusion coefficients of the molecules from the mean-square-displacement (MSD) of particle centres of mass using the following Einstein relation:

$$D=\frac{1}{6}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{dt}}\left\langle\sum_{u=1}^{N}[\vec{r}_i(t)-\vec{r}_i(0)]^2\right\rangle$$

Calculation of the Thermal conductivity λ (defined as the linear coefficient relating the macroscopic heat current to the temperature gradient according to the Fourier's law: $\mathbf{J}=-\lambda\nabla T$, through the Green-Kubo formula:

$$\lambda=\frac{1}{3Vk_BT^2}\int_0^\infty\left\langle\mathbf{j}(0)\mathbf{j}(t)\right\rangle dt$$

where V is the volume and T the temperature. Angular brackets denote the average over time. The factor 3 accounts for averaging over 3 dimensions. The microscopic heat current is given by:

$$\mathbf{j}(t)=\sum_i\mathbf{v}_i e_i+\frac{1}{2}\sum_{i<j}\mathbf{r}_{ij}\left[\mathbf{F}_{ij}\cdot\left(\mathbf{v}_i+\mathbf{v}_j\right)\right]$$

$\boldsymbol{v}_i$ is the velocity of particle *i* and $\boldsymbol{F}_{ij}$ is the force on atom *i* due to its neighbour *j* from pairwise potential (an alternative formulation for ab-initio calculations, where the forces are not pairwise, is being devised).

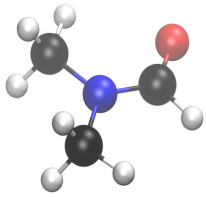

Figure 1- Dimethylformamide (DMF)

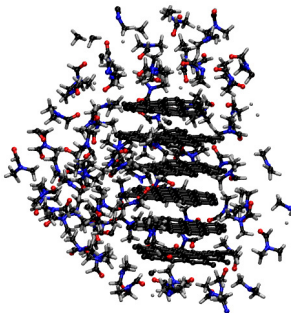

Figure 2- Nanographite system formed by 6 layers of graphene of 16 benzene rings each, in DMF.

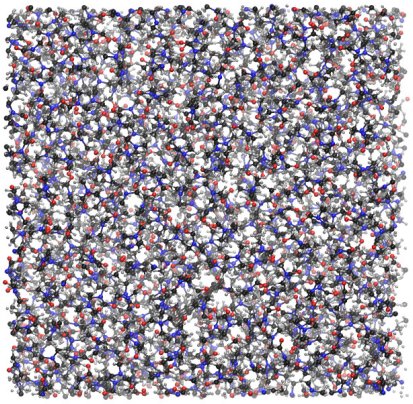

Figure 3 - Nanographene with 9 benzene rings (inside the red circle) in DMF.

**Achievements**

We have started testing this protocol for a nanofluid composed of an organic solvent (dimethylformamide - DMF), with graphite nanoflakes disolved (staks of graphene layers with a few Å or nm in diameter). These nanofluids are being used for experimental studies by the group of Prof. Pedro Gomez at ICN2, and they will serve as a test bed for our algorithms and protocols. So far, we have reached these milestones:

A1 The densities of the homogenous systems (water, ethanol and DMF) have been evaluated and found in very good agreement with the experimental results, supporting our choice for the setup in molecular dynamics.

A2 The first evaluations of heat capacities of the homogenous and heterogenous systems (graphene/graphite-like of different sizes) have been completed, shows an certain increase of $C_p$ the nanofluids compared with the solvent.

A3 The evaluation of the self-diffusion coefficients for the system particles shows in some cases a slower mobility with respect to the experimental results.

A4 Our preliminary calculations on the thermal conductivity calculated for the homogenous system (DMF) are in very good agreement with experimental results.

**Outlook for the future**

- Writing and documenting the protocol for production to calculate the thermal properties.
- Implementation and test the high-throughput procedure to apply the workflow of our protocol using the AIIDA infrastructure developed within the MaX consortium.
- Evaluation and full study of the thermal properties of nanographene systems dispersed in DMF.
- Application to molten salts without and with nanoparticles.
- Feedback from Abengoa Research and possible modifications and improvements in the protocol.

## Pilot Case 3. Computational protocol for simulating the colour optical properties of natural dyes for food-industry applications (Key Person: S. Baroni, SISSA, in collaboration with Mars Chocolate).

**Industrial Interest**

In order to comply with EU regulations on food safety, many colorants commonly employed in the food industry will be substituted with natural ones. However, the colour palette from natural sources is still incomplete, and the understanding of the relation between the chemical structure and the optical properties of natural pigments inadequate, thus making the chase of molecules with custom-designated chromatic properties a blind search.

**Target**

We aim at designing and implementing a simulation protocol to assist industrial research in the identification of the most suitable natural dyes to express custom-designated hues of colours (particularly in the purple-blue gamut), and to apply it to the screening of anthocyanins (see Figure 1).

**The protocol**

1. A classical molecular-dynamics (MD) module, including an innovative clustering algorithm and enhanced to achieve quantum-mechanical accuracy, aimed at identifying and classifying different molecular conformers, according to the relative probability of their occurrence in solution.
2. An AIMD module aimed at sampling the relevant thermal fluctuations within each conformer identified at point 1.
3. A quantum spectroscopy module, aimed at evaluating the optical spectra for each molecular configuration sampled by AIMD according to point 2.

All this implemented in the Quantum ESPRESSO suite of computer codes, interfaced with the GROMACS bio-molecular modelling package.

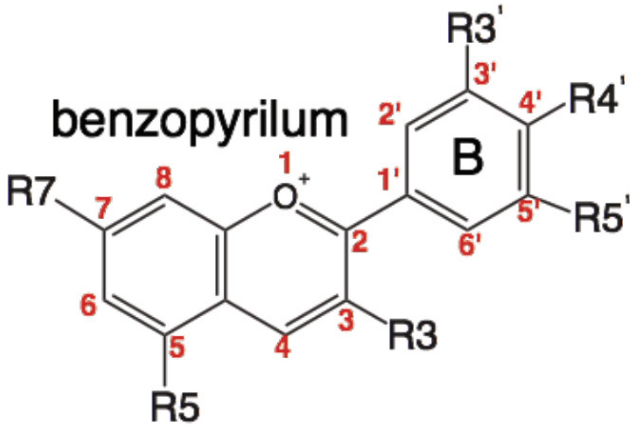


Figure 1 – General chemical structure of anthocyanins.

**Achievements**

**A1** Development, implementation, and validation of a novel algorithm to identify the dominant molecular conformers of complex molecular systems in solution.
Marta Rosa, Marco Micciarelli, Alessandro Laio, and Stefano Baroni, Sampling molecular conformers in solution with quantum mechanical accuracy at a nearly molecular mechanics cost, submitted for publication.

**A2** Development, implementation, and validation of a Self Consistent Continuum Solvation Model to compute TDDFT molecular spectra in solution.
Iurii Timrov, Marco Micciarelli, Marta Rosa, Arrigo Calzolari, and Stefano Baroni Multi-model approach to the optical properties of molecular dyes in solution, submitted for publication.

**A3** Development, implementation, and validation of a learn-on-the-y technique to enhance the large-scale dynamical sampling of TDDFT molecular spectra. Sampling molecular spectra dynamically requires the repeated solution of Casida's equation along a MD trajectory, a very demanding endeavour, particularly when using hybrid functionals and plane-wave basis sets. In many systems, including anthocyanins, TDDFT spectra are significantly different but qualitatively similar to the independent-electron spectra, which are much less expensive to compute. We have devised a learn on the y technique that allows to efficiently and accurately interpolate between TDDFT spectra computed once in while along a MD run, using independent-electron ingredients sampled whenever they are needed. A paper on this methodology is currently in preparation.

**A4** An MPI implementation QM/MM molecular dynamics in Quantum ESPRESSO QM/MM molecular dynamics was implemented in Quantum ESPRESSO using a socket- based interface between its pw.x module and the LAMMPS package for classical MD simulations. While technically sweet, this implementation is not well suited to massively parallel architectures and has severe limitations in what concerns portability and ease of use. The QM/MM module in Quantum ESPRESSO, has been refurbished from ground up and is ready for distribution with the 5.4 release, featuring a single (parallel) executable running both the MM and the QM codes, which trade data and communicate via MPI.

**A5** Implementation of a graphical post-processing tool to analyse and visualize molecular spectra. The post-processing tool is (so far) capable of:

- Calculating colours in different representations (RGB, XYZ, etc.) starting from absorption spectra;
- Easily plotting many different spectra (corresponding to different frames along an
- MD trajectory) and represent each of them with its own perceived colour;
- Mounting the different plots in a movie representing the optical behaviour of the solution.

**A6** Application and benchmark of the simulation protocol:

- Application of the entire protocol for thorough colour simulation in cyanin (cyaninidin- 3-glucoside): classification of the molecular conformers by cluster analysis → AIMD of most relevant conformers → TDDFT absorption spectrum → perceived colour for the cyanin in its positive (avylium cation, AH+), neutral (quinonoidal base, A), and negative (AH-) protonation states, which are stable at different acidic conditions.
- Preliminary identification and characterisation of possible structural modification favouring the hue of colour desired by the industrial partners for the case of cyanin.
- Application of the classical module of the protocol to more complex (large) antho-cyanins to identify conformational differences due to structural modifications that can favour the hue of colour desired by the industrial partners.

**Outlook for the future**

- Deployment of QM/MM for production
- Implementation and test of a high-throughput procedure to apply the workow of our multi-scale protocol using the AiiDA infrastructure developed within the MaX consortium.

The multi-scale protocol is ready to be utilised for:

- Structural, electronic, and spectroscopic characterization of complex anthocyanins (>150 atoms) in solution;
- Modelling the effects of metal (Fe, Al) co-pigmentation;
- Extension to sugar-water (syrup) solutions;
- Simulation of the de-protonation process and determination of the acid dissociation constant, $pK_a$, of select co-pigments;
- Enhancement of our simulation protocol with a machine-learning module to identify correlations between structural and optical fluctuations in the dynamics of solvated anthocyanins; Respond to specific simulation/modelling/interpretation needs that may arise as a result of the collaboration between industrial experimental partners.

## Pilot Case 4. Design and discovery of optimal solid-state electrolytes (Key Person: N. Marzari, EPFL, in collaboration with the Bosch Research and Technology Center).

### Introduction

In order to drastically reduce the amount of greenhouse gases emitted by our vehicle fleets, a substantial improvement in performance and safety of electrochemical storage systems is mandatory. This can only be achieved by finding new materials for solid-state electrolytes for lithium ions and protons in a high-throughput screening approach. In order to get there, we need to understand diffusion processes and find descriptors for ionic conductivity, which is the key step for any material screening approach. The present report summarizes our efforts to tackle this ambitious problem.

### Descriptors search

We are currently screening 1207 Li-containing oxides for their suitability as solid-state electrolytes in Li-ion batteries, downloaded from the “materials project” database. A first search for descriptors has been performed via a newly developed algorithm, which we call the “pinball model”, where lithium carriers diffuse in a frozen energy landscape defined by the material’s rigid matrix. This approximation permits to simulate diffusion by molecular dynamics in a very fast way. A typical result is shown in fig. 1.

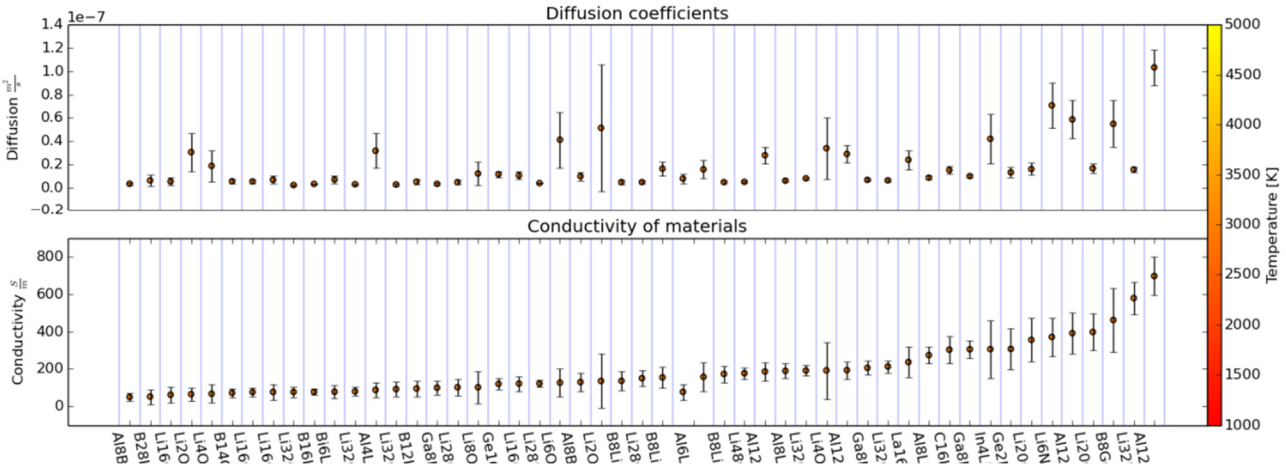


Fig1. Typical results of a pinball computation, where materials are sorted by the conductivity value

As a next step, we are going to analyse the performed runs and select the most promising materials to study using more accurate ab initio molecular dynamics simulations.

We also implemented algorithms based on the Delaunay Triangulation on crystal structures to detect conductivity pathways in materials (illustrated in fig. 2). We expect that this framework enables us to detect good conductors from relatively

short molecular dynamics simulations. Additionally, by correlating observables such as site volume and chemical environment with the transition rates observed in molecular dynamics simulations, we are augmenting our understanding of diffusion in solid state.

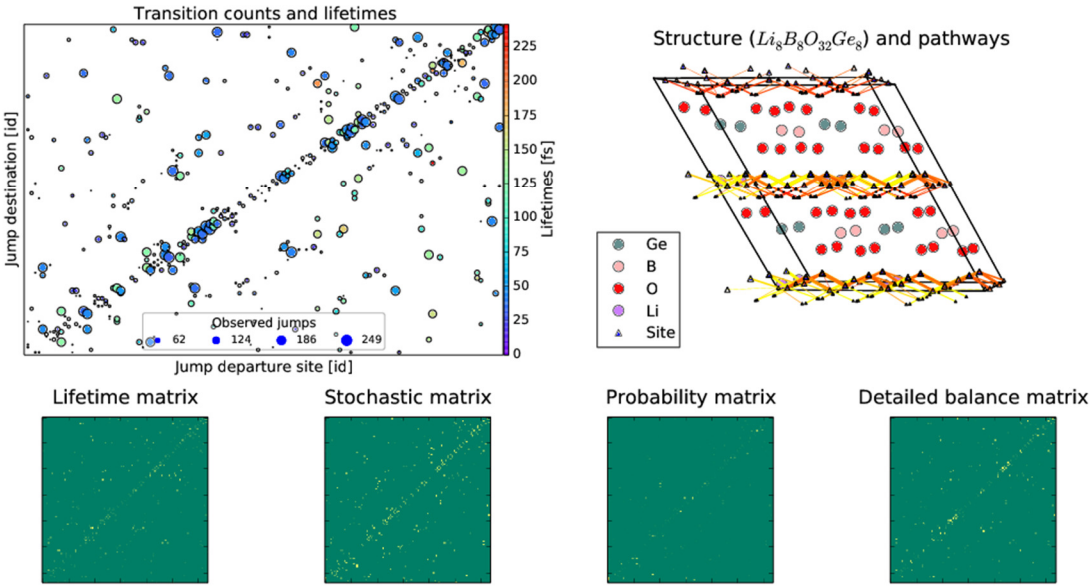


Fig2: Typical result of a Delaunay triangulation combined with molecular dynamics simulation.

**Aiida framework**

High-throughput materials screening -- such as our search for novel ionic conductors -- can only be done with the appropriate tools enabling scientists to launch complex workflows and record the provenance of the results. To meet these requirements, we worked on a prototype of a new workflow manager that is currently being implemented in the Aiida framework, a platform for high-throughput materials simulation. With this new engine, we have a powerful tool to easily run workflows such as the one shown in fig. 3 and test our descriptors on an unequalled number of structures.

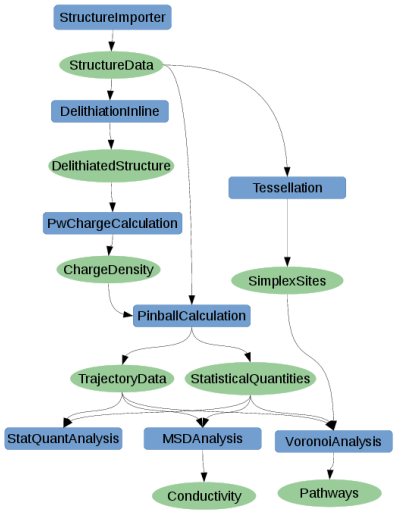


Fig3: Example of an Aiida workflow.

**Next steps**

The most promising materials provided by the “pinball” technique have to be validated against more accurate and costly simulations to understand the model’s predictive power and eventually to improve it, thus creating a positive feedback loop in our material’s research . We understood that the role of phonons of the rigid matrix is a key ingredient; therefore, one line of research will

be devoted to including this type of physics into the pinball model and perform further screening considering these effects. The Aiida platform will be the major computational tool used at this stage.

**References**

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