

Hydrogen storage in MgH₂ matrices: a study of Mg-MgH₂ interface using Car-Parrinello molecular dynamics code on ENEA-GRID.

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Introduction

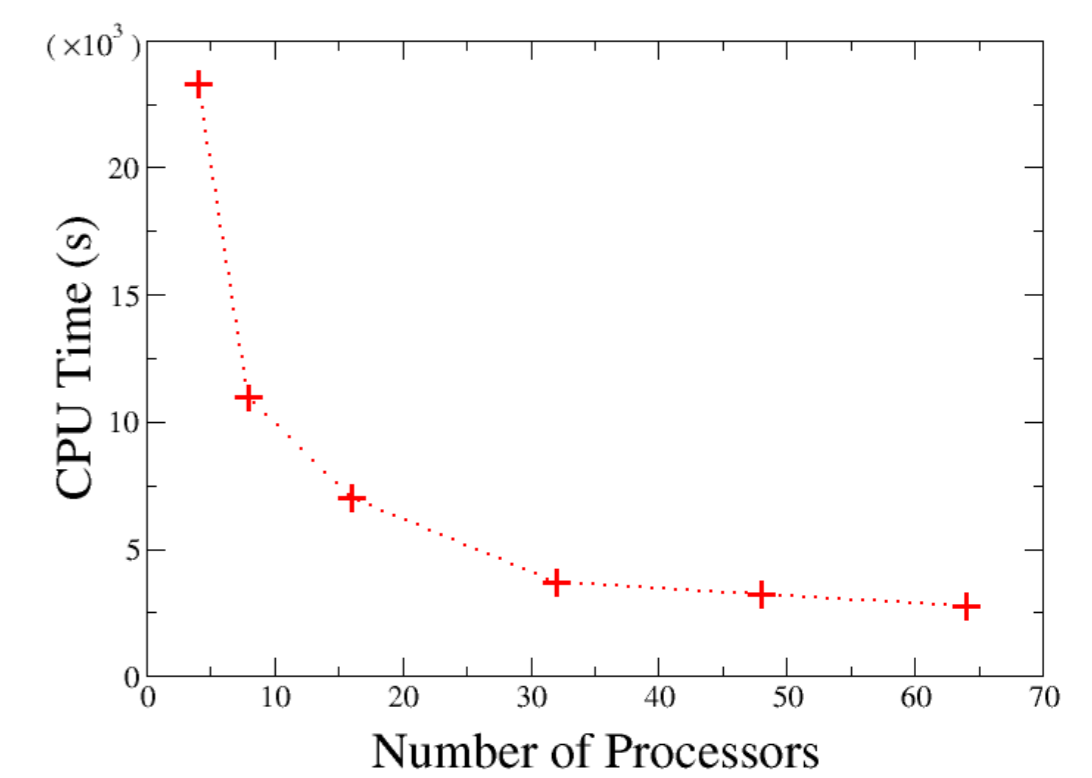
The remarkable ability of magnesium to store significant quantities of hydrogen has fostered intense research efforts in the last years in view of its future applications where light and safe hydrogen-storage media are needed. Magnesium material, characterized by light weight and low cost of production, can reversibly store about 7.7 wt% hydrogen (MgH₂). However, further research is needed since Mg has a high operation temperature and slow absorption kinetics that prevent for the moment the use in practical applications. For these reasons a detailed study of the interface between Mg and MgH₂ is needed to characterize the dynamics of hydrogen at the interface. Further insights are gained by characterizing and comparing the Mg-MgH₂ interfaces which are supposed to play a major role in the hydrogen diffusion during absorption and desorption cycles. From an experimental point of view there is not a clear evidence of which interfaces are involved in the hydrogen diffusion and which is the atomic dynamics at the interfaces. By means of accurate *ab-initio* molecular dynamics simulations based on the density-functional theory with norm-conserving pseudopotentials and plane-wave expansion (CPMD code) an interface is reproduced and studied. Extensive electronic structure calculations are used to characterize the equilibrium properties and the behavior of the surfaces in terms of total energy considerations and atomic diffusion.

CPMD code

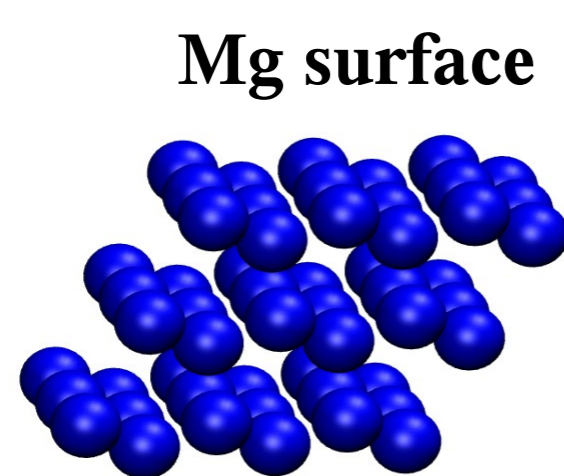
CPMD is an *ab-initio* electronic structure and molecular dynamics (MD) program using a plane wave/pseudopotential implementation of density functional theory. It is mainly targeted at Car-Parrinello MD simulations, but also supports geometry optimizations, Born-Oppenheimer MD, path integral MD, response functions, excited states and calculation of some electronic properties. In *ab-initio* Molecular Dynamics simulation, the forces acting on atoms are calculated from an electronic structure calculation repeated every time step ("on the fly"). Thanks to electronic structure calculation by using Density Functional methods, simulations of large systems with hundreds of atoms are now standard. Originally developed by Roberto Car and Michele Parrinello for applications in solid state physics and material science, this method has also been used with great success for the study of molecular systems. Applications of *ab-initio* Car-Parrinello Molecular Dynamics simulations range from the thermodynamics of solids and liquids to the study of chemical reactions in solution and on metal and oxide surfaces. CPMD code runs on many different computer architectures and allows good scalability till a large number of processors depending on the system size.

Parallelization Benchmark

We test the CPMD code for the system showed in this poster that represent a Mg-MgH₂ interface constituted by 88 atoms of magnesium and 80 atoms of hydrogen. We use a CPMD (version 3.11.1) code compiled on IBM architecture with MPI parallelization, and exploit the Power5 IBM CPUs (1.5 GHz). In the figure in side we show the total time required by the code to perform 300 molecular dynamics time steps using increasing number of processors (from 4 up to 64). Every nodes is set up by 16 CPUs. The benchmark results demonstrate the high performance of the parallelization on Power5 CPUs for floating point intensive applications and the good scalability up 64 processors.



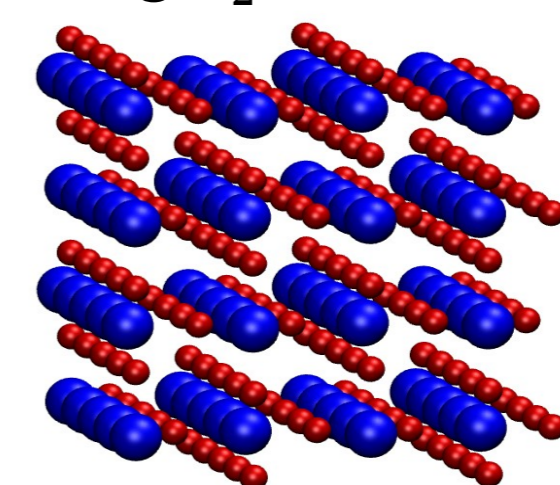
Surfaces



The only surfaces satisfying the periodic boundary conditions in the atomic configuration with the interface are: [010] for Mg and [110] for MgH₂

- Mg atom
- H atom

MgH₂ surface

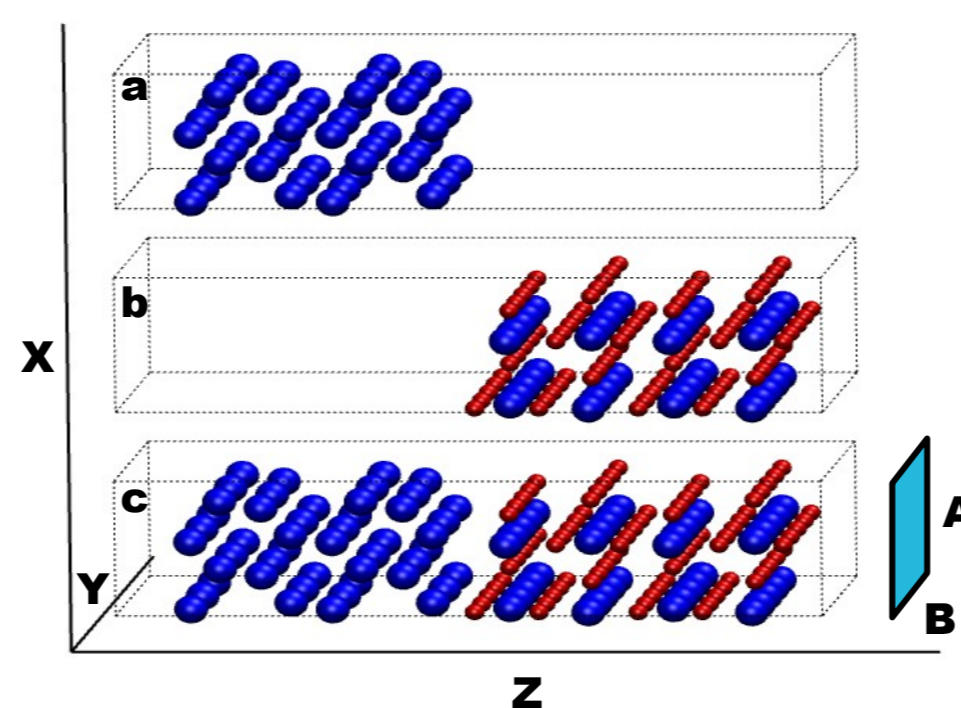


Interface

- a) Mg surface: 48 Mg atoms;
- b) MgH₂ surface: 40 Mg and 80 H atoms;
- c) Mg-MgH₂ interface: 88 Mg and 80 H atoms.

Periodic boundary conditions are kept in the x and y direction.

In the z direction the c) atomic system is composed by two free surfaces and one interface. Free surfaces are the same surfaces composing the interface but translated in the xy plane.



Work of adhesion per unit area is the work done on the system when two condensed phases, forming an interface of unit area, are separated reversibly to form two non-interacting free surfaces:

$$E_{\text{inter}} = E_{\text{MgH}_2} + E_{\text{Mg}} - E_{\text{tot}} = 310 \text{ mJ/m}^2$$

$$L_x = 6.2094 \text{ \AA}; L_y = 15.089 \text{ \AA}; L_z = 38.697 \text{ \AA}$$

NVT molecular dynamics

Constant temperature and constant volume *ab-initio* molecular dynamics simulations (using the CPMD code) are performed from room temperature to 900 K for system (c). Atoms on the free surfaces in the system (c) are kept fixed to mimic bulk behavior and to minimize interactions among the interface and the free surfaces. The final configurations reveal an increased mobility of hydrogen atoms near the interface. This mobility is much higher than for bulk hydrogen atoms. This difference increases at higher temperatures. No hydrogen atoms are observed to diffuse in the Mg bulk.

