Supplementary material:

Summary of the Car-Parrinello method.

The Car-Parrinello molecular dynamics method[1,2] relies on the following extended Lagrangian:

$$L^{CP}\left(c,\dot{c},R,\dot{R}\right)=\mu\sum_{i,G}\dot{c}_i*(G)\dot{c}_i(G)+\frac{1}{2}\sum_I \dot{R}_I^2-E^{KS}(c,R)+\sum_{i,j}\Lambda_{ij}\left[\sum_G c_i(G)\dot{c}_j(G)-\delta_{ij}\right]$$

where the Kohn-Sham one-electron orbitals have been expanded on a plane-wave basis set as

$$\phi_i(\vec{r})=\sum_G c_i(\vec{G})\frac{1}{\sqrt{\Omega}}e^{-i\vec{G}.\vec{r}}$$

and the ground state electronic density is

$$n(r)=\sum_i\left|\phi_i(r)\right|^2.$$

Ω is the volume of the simulation box, and for an orthorhombic box with lengths L_x, L_y, L_z, wavevectors $\vec{G}$ are

$$\vec{G}=i\frac{2\pi}{L_x}\vec{x}+j\frac{2\pi}{L_y}\vec{y}+k\frac{2\pi}{L_z}\vec{z}$$

with $(i,j,k)\in\Xi$ and $(\vec{x},\vec{y},\vec{z})$ unitary vectors. $\dot{c}_i(\vec{G})$ are the time derivatives of $c_i(\vec{G})$, and $c_i*(\vec{G})$ complex conjugates. $E^{KS}(c, R)$ is the Kohn-Sham energy.

The plane-wave expansion is carried over up to a cut-off energy E_{cut}, giving a number of plane-waves

$N_{PW}\approx\frac{1}{2\pi^2}\Omega E_{cut}^{3/2}$ (basis set size). Note that pseudo-potentials are needed in order to limit the number of plane-waves.

In the Car-Parrinello formalism, $c_i(\vec{G})$ coefficients are considered as additional degrees of freedom, which are assigned a fictitious mass μ (commonly referred as the fictitious electron mass). R_I and $\dot{R}_I$ are respectively the positions and velocities of atom I (mass M_I). The potential energy of the system is $E(c,R)$ which is the electron+nuclei total energy in the Kohn-Sham framework. Λ_{ij} are Lagrange multipliers that satisfy the orthonormality constraints of the Kohn-Sham orbitals.

The following set of coupled equations of motions is obtained under the orthonormality constraints:

$$\mu\ddot{c}_i(\vec{G})=-\frac{\partial E(c,R)}{\partial c_i*(\vec{G})}+\sum_j\Lambda_{ij}c_j(\vec{G})$$

$$M_I\ddot{R}_I=-\frac{\partial E(c,R)}{\partial R_I}$$

A velocity Verlet algorithm is used to solve the coupled equations of motion, which propagates simultaneously the nuclei positions and the electronic degrees of freedom.

The Car-Parrinello Hamiltonian conserved along microcanonical NVE trajectories is:

$$H^{CP}\left(c,\dot{c},R,\dot{R}\right)=\mu\sum_{i,G}\dot{c}_i*(\vec{G})\dot{c}_i(\vec{G})+\frac{1}{2}\sum_I M_I\dot{R}_I^2+E(c,R).$$

We emphasize once more that Car-Parrinello (CP) dynamics are not Born-Oppenheimer (BO) dynamics. In the latter case, optimization of the wave-function is done at each time step of the dynamics, for a given configuration of the nuclei. In CP dynamics, the wave-function is optimized once at the beginning of the simulation, and is subsequently time-propagated simultaneously to the nuclei dynamics. Choice of the fictitious electron mass is therefore crucial in order to assure that the electrons respond adiabatically to the forces from the nuclei, and assure that the CP electronic state stays close to the 'true' BO surface. We refer the reader to references[3,4] for a rigorous mathematical justification. In practice, allowed values of μ range between 100 and 500 a.m.u. for typical molecular systems containing C, N, O, and H atoms. We refer to references[5-7] for more information about this subject.

Simulations are usually done under periodic boundary conditions (PBC). Decoupling techniques[8] can be applied in order to eliminate the effect of the periodic images of the charge density. In that case, "gas phase" simulations can be performed.

Parameters:

The DFT-based Car-Parrinello simulations performed in this work follow the general set-up:

–Becke, Lee, Yang and Parr (BLYP) gradient-corrected functional for the exchange and correlation terms.

–The one-electron orbitals are expanded in a plane-wave basis set with a kinetic energy cut-off of 70 Ry restricted to the gamma point of the Brillouin zone.

–Medium soft norm-conserving pseudopotentials of the Martins-Trouillier type[9] are used.

–The core-valence interaction of C, N and O is treated by s and p potentials with pseudization radii of 1.23, 1.12 and 1.05 a.u., respectively (taking the same radius for s and p), while H atoms are treated as a s potential with a 0.5 a.u. radius.

–Energy expectations are calculated in reciprocal space using the Kleinman-Bylander transformation.[10]

–The fictitious electron mass is 500 a.u. and the time step is 5 a.u. (0.12 femtoseconds)

–A cubic box length of 20 Angstroms has been used for the molecular dynamics of Ala-Ala-H+ peptide and RGD. Prescriptions for the choice of the box length have been reported in our previous reference.[11]

–Microcanonical dynamics have been performed, i.e. without any rescaling of temperature nor application of thermostats

–The decoupling technique of Martyna and Tuckerman[12] has been applied in order to eliminate the effect of the periodic images of the charge density.

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