

## Efficient mixed-force first-principles molecular dynamics

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We present an efficient method to mix well converged *ab initio* forces with simpler and faster ones in molecular dynamics. While the cheap forces are evaluated every time step, the converged ones correct the trajectory only every  $n$  time steps. For convenience, both types of forces are calculated with the same basic scheme, using density functional theory, norm-conserving pseudopotentials, and a basis set of numerical atomic orbitals. The cheap forces are evaluated with a short-range minimal basis set and the non-self-consistent Harris functional. Since these evaluations are hundreds of times faster than those of the converged forces, they add a negligible cost, and the boost in computational efficiency is approximately a factor  $n$ . Our results indicate that one can use values of  $n$  of up to 10, without affecting significantly the calculated structural and dynamical magnitudes.

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Molecular dynamics (MD) is a fundamental tool in atomic materials simulation [1]. A majority of practitioners have used classical, semiempirical interatomic potentials. This is necessary for the large sizes and long times required to simulate many processes of enormous scientific and technological interest, from materials deformation and fracture [2] to protein folding [3]. A large effort has been devoted to develop interatomic potentials for many types of systems [4]. However, the quantitative reliability of such potentials in situations of bond formation and breaking is highly questionable. In such cases, it is imperative to use the much more expensive *ab initio* MD methods [5,6], generally limited to a few hundred atoms and a few tens of picoseconds. Thus, it is essential to find methods that accelerate the integration of the dynamical equations, thus allowing for longer simulations.

In classical dynamics, one of such methods [7] uses multiple time scales to integrate the equations of motion for systems with both fast and slow dynamical degrees of freedom. The same method can be used to compute separately the hard, short-ranged forces from the soft, long-ranged ones. De Vita and Car [8] have proposed to adapt “on the fly” the parameters of a classical potential using sporadic or periodic evaluations of *ab initio* forces. In this work, drawing ideas of those previous works, we propose a simple method to speed up dramatically *ab initio* MD. In principle, it could be implemented by combining classical and *ab initio* forces. However, such an approach would still require to develop a suitable classical force field for every new system with different interactions. Therefore, instead we take advantage of the fact that, while standard density functional forces require the simultaneous convergence of many parameters, much lower values of those parameters can still yield quite reasonable forces. Thus, by reducing drastically the size of the basis set, the Brillouin zone sampling, or the number of self-consistency iterations, it is possible to reduce the computer time by enormous factors and still obtain forces that are considerably more reliable than those of classical interatomic potentials.

To test our scheme, we have chosen the SIESTA method [9,10], which is specially well suited to span the range from

“quick and dirty” calculations to fully converged ones. It uses density functional theory [11], norm-conserving pseudopotentials [12] and a basis set of numerical atomic orbitals of strictly finite range [13,14]. To calculate converged forces, we might typically use the generalized gradient approximation to exchange and correlation (with spin polarization if required), double- $\zeta$  polarized (DZP) basis orbitals with a relatively long range, fine integration grids in real and reciprocal space, and a well converged self-consistency between density and potential. For the cheap forces we may save on many different parameters, depending on the system and the properties studied. Thus, we may use the local density approximation (LDA), a minimal single- $\zeta$  basis set with short range, a coarser integration grid in real space, just the  $\Gamma$

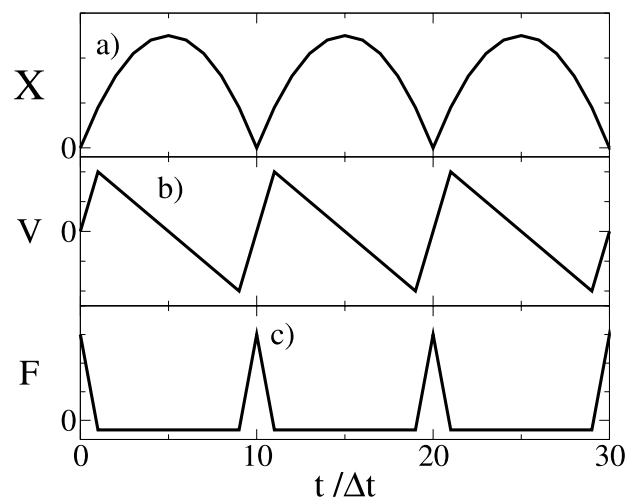


FIG. 1. Schematic (a) position, (b) velocity, and (c) force, in arbitrary units, for a particle moving in one dimension, generated by the mixed-force algorithm with zero initial velocity and a force correction interval of ten time steps. For simplicity, the converged force is equal to zero and the cheap (fast) force is a negative constant. The periodic force correction kicks are positive and invert the velocity. Notice that the position and velocity at the correction steps are equal to their correct converged value (zero).

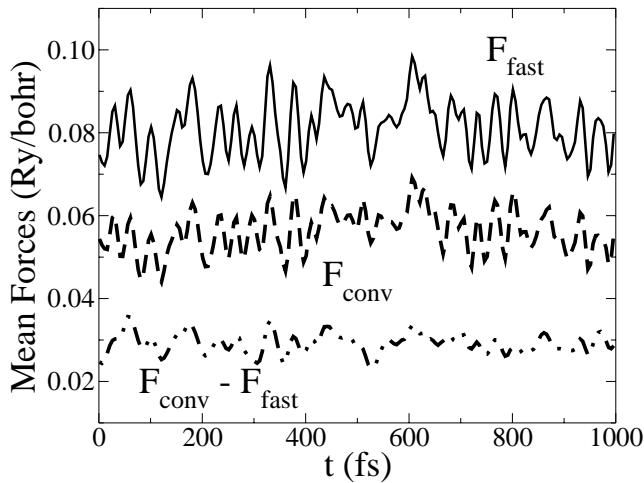


FIG. 2. Decomposition of the total converged forces  $\mathbf{F}_{conv}$  into a cheaply evaluated component  $\mathbf{F}_{fast}$ , and a remainder  $\mathbf{F}_{conv} - \mathbf{F}_{fast}$ . Represented are the average norms as a function of time. The trajectory was generated for 64 Si atoms at 2000 K, using the converged forces.

point in reciprocal space, and the non-self-consistent Harris functional [15]. Altogether the cheap forces are typically hundreds of times faster to compute than the converged ones, and therefore they add a negligible cost to the overall calculation, thus making it unnecessary to resort to classical force fields.

As usual, we use the Born-Oppenheimer approximation and we treat the nuclei as classical particles, subject to the Hellmann-Feynman forces (including all Pulay corrections). The equations of motion are solved with the standard velocity-Verlet algorithm [1], which ensures the time reversibility of the trajectories [7]. The atomic forces at time  $t$  are defined as  $\mathbf{F}_{fast}(t) + \Delta\mathbf{F}(t)$ , where

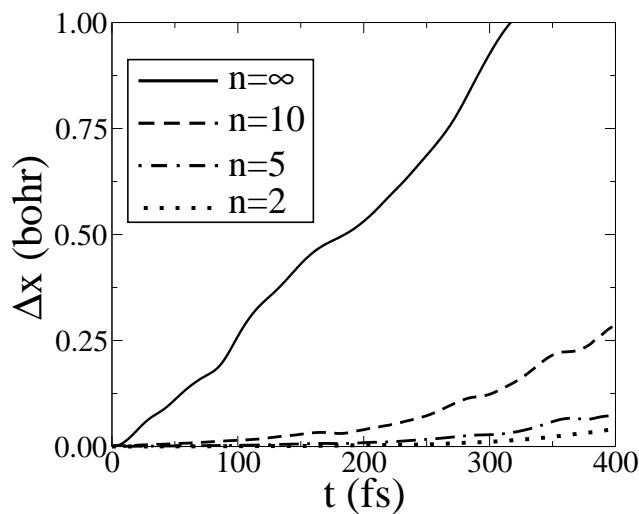


FIG. 3. Divergence of the mixed-force MD trajectories from the converged-force trajectory for the liquid silicon system.  $\Delta x$  is the average distance in atomic positions between the given and the reference trajectories. Force corrections were made every  $n = 2, 5, 10$ , and  $\infty$  (only fast forces) time steps.

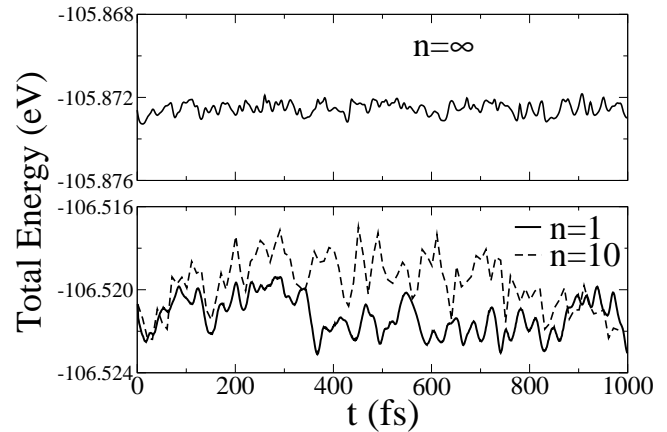


FIG. 4. Total energy per atom as a function of time for the liquid silicon system. In the mixed-force ( $n=10$ ) and converged-force ( $n=1$ ) trajectories, the total energy was calculated at the correction steps, as the sum of the Kohn-Sham energy plus the nuclear repulsion and kinetic energies. In the fast-force trajectory ( $n=\infty$ ), it was calculated at every step, using the Harris-functional for the electronic part. The standard deviations are 0.9, 1.3, and 0.3 meV/atom for the  $n=1, 10$ , and  $\infty$  trajectories, respectively.

$$\Delta\mathbf{F}(t) = \begin{cases} n[\mathbf{F}_{conv}(t) - \mathbf{F}_{fast}(t)] & \text{if } (t/\Delta t \bmod n) = 0 \\ 0 & \text{otherwise.} \end{cases} \quad (1)$$

Thus, the expensive converged forces  $\mathbf{F}_{conv}$  need to be evaluated only once every  $n$  time steps  $\Delta t$ . In those “correction steps,” the trajectories generated by the cheap (fast) forces  $\mathbf{F}_{fast}$  are corrected by applying a force “kick” equal to the difference between the converged and fast forces at that time, multiplied by  $n$ . The factor  $n$  accounts for the concentration of the continuous force correction  $\mathbf{F}_{conv}(t) - \mathbf{F}_{fast}(t)$  in one out of every  $n$  steps. The method of Ref. [16], based on the position-Verlet algorithm, was reported to have a better numerical stability in response to the correction kicks. The efficiency of that method in the present context will be studied in future works.

Figure 1 shows schematically the positions, velocities, and forces of a particle moving in one dimension, generated with our mixed-force algorithm. For simplicity, we take the converged force and the initial velocity equal to zero, so that the correct converged position is also zero at all times. The mixed-force trajectory, for a constant negative fast force, shows periodic force kicks that change discontinuously the velocity and invert the trajectory at the correction steps.

We have applied this method to simulate a system of 64 silicon atoms at an average temperature of  $\sim 2000$  K and an average pressure close to zero. This high temperature was intentionally chosen to test the method under specially stringent conditions, with high kinetic energies and frequent formation and breaking of bonds. The simulations were performed with the SIESTA program [10] but standard Hamiltonian diagonalizations were used instead of order- $N$  methods [17,18], because of the metallic character of liquid silicon. For the cheap forces we use the Harris functional, a minimal basis set with a range of 3.5 and 4.0 bohr for  $s$  and

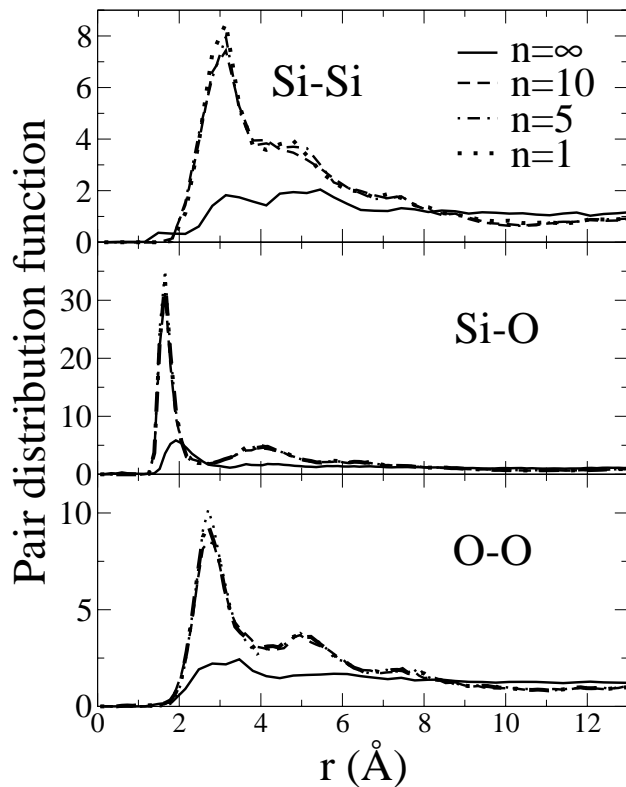


FIG. 5. Radial pair distribution functions of liquid  $\text{SiO}_2$  at 5500 K, using the new method with different values of  $n$ . The converged forces, used for  $n=1$  and for the correction steps of  $n=5$  and 10, were obtained with a double  $\zeta$  plus polarization basis set, a real-space grid with a plane wave cutoff of 200 Ry, and only the  $\Gamma$   $k$  point. The fast forces (that yield the  $n=\infty$  curves when uncorrected) were calculated with a minimal basis set (single  $\zeta$ ), a real-space grid with a plane wave cutoff of 150 Ry, and only the  $\Gamma$   $k$  point.

$p$  orbitals, a real-space integration grid with a plane wave cutoff of 40 Ry, and only the  $\Gamma$   $k$  point. For the converged forces, we use the self-consistent Kohn-Sham functional in the LDA, a DZP basis set with a range of 5.4, 6.5, and 3.8 for  $s$ ,  $p$ , and  $d$  basis orbitals, a real-space grid with a 80-Ry plane wave cutoff, and only the  $\Gamma$   $k$  point. The forces are corrected according to Eq. (1) every  $n$  time steps, with  $\Delta t = 1$  fs.

Figure 2 compares the magnitudes of the fast and converged forces, and of their difference. It can be seen that the latter is a relatively small and smooth correction, which explains why it may be evaluated and applied less frequently.

Figure 3 represents the divergence of the trajectories, generated with different values of  $n$ , away from the reference converged trajectory [which corresponds to  $n=1$  in Eq. (1)]. It can be seen that even the  $n=10$  trajectory diverges much more slowly than that obtained purely from the fast forces (labeled  $n=\infty$ , i.e., with no force corrections).

Figure 4 shows the total energy as a function of time. The energy conservation is considerably worse in the self-consistent converged-force trajectory ( $n=1$ ) than in the Harris-force trajectory ( $n=\infty$ ). This probably reflects larger effects of charge sloshings and analytic discontinuities in the

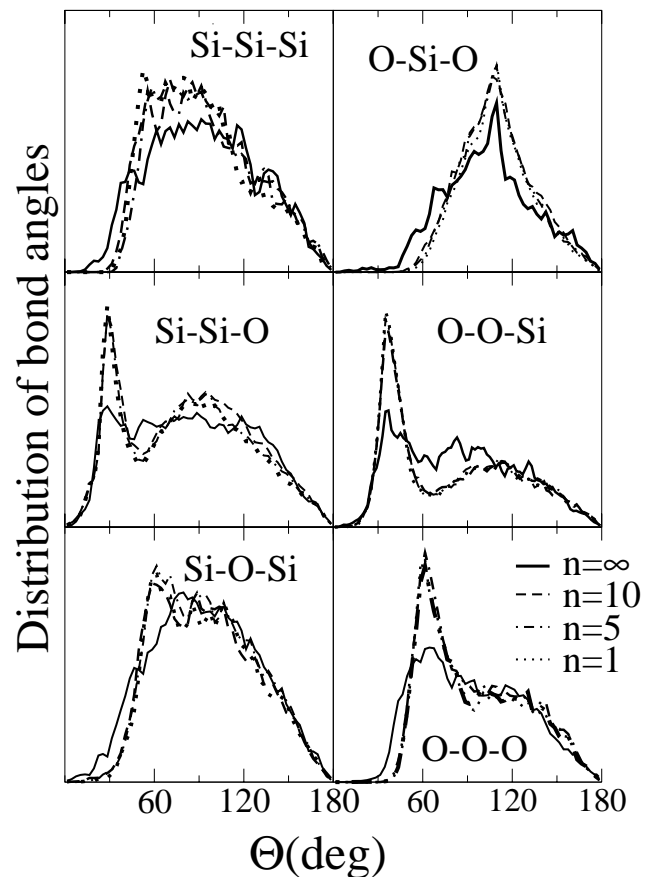


FIG. 6. Bond-angle distribution functions of the liquid  $\text{SiO}_2$  system, using the new method with different values of  $n$ . The bond cutoff radii were chosen 10% larger than the first maximum in the corresponding pair distribution functions of Fig. 5.

forces due to frequent level crossings in this highly disordered system. However, it is important to notice that the energy conservation in the mixed-force trajectory ( $n=10$ ) is similar to that in the converged trajectory.

Despite the high simulation temperature, the charge transfer in elemental liquid silicon may be expected to be considerably smaller than in an ionic system, making the non-self-consistent Harris functional specially adequate. In fact, we have seen that structural magnitudes such as the bond length and bond-angle distributions are not very different using the Kohn-Sham and Harris functionals. Therefore, we have also studied a more challenging system, liquid silica, using 72 atoms at a high average temperature of 5500 K and a low density of  $0.42 \text{ g/cm}^3$ , typical of porous silica aerogels [19]. The distributions of bond lengths and angles, presented in Figs. 5 and 6, are indeed very different using the two functionals ( $n=1$  and  $n=\infty$ ). Despite this, the mixed-force method, with up to  $n=10$ , yields the same distributions, within the statistical noise, as the converged Kohn-Sham trajectory. Similar results, to be presented elsewhere, were obtained for an even more ionic system, liquid magnesium oxide, with 54 atoms at 6500 K and 30 GPa.

It might be expected that dynamical magnitudes are more sensitive than thermodynamic averages to changes in how the MD trajectories are obtained. Figure 7 shows the velocity

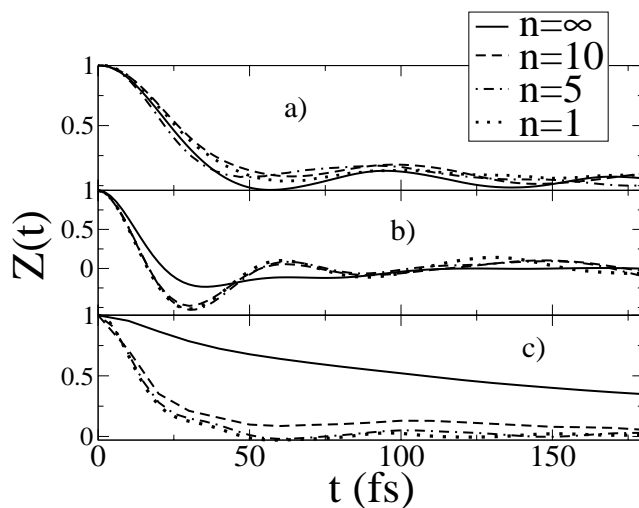


FIG. 7. Velocity autocorrelation function  $Z(t) = \langle \mathbf{v}_i(t') \mathbf{v}_i(t'+t) \rangle / \langle \mathbf{v}_i^2(t') \rangle$  as a function of the interval  $n$  between force corrections, for (a) liquid Si at 2000 K and zero pressure, (b) liquid MgO at 6500 K and 30 GPa, and (c) liquid SiO<sub>2</sub> at 5500 K and a density of 0.42 g/cm<sup>3</sup>.

autocorrelation function for the three systems studied, as a function of the interval  $n$  between force corrections. As expected, the trajectory of the non-self-consistent Harris functional is reasonably accurate only for elemental liquid sili-

con. But, in every case, the mixed-force method, with up to  $n = 10$ , yields essentially the same velocity autocorrelations as the converged Kohn-Sham trajectories. We have also calculated self-diffusion coefficients from the average quadratic distances traversed as a function of time. Thus, for liquid silicon we obtain, respectively  $(2.4 \pm 0.1)$ ,  $(2.5 \pm 0.1)$ ,  $(2.6 \pm 0.1)$ ,  $(2.6 \pm 0.1)$ , and  $(2.0 \pm 0.1) \times 10^{-4}$  cm<sup>2</sup>/s for  $n = 1, 5, 10, 20$ , and  $\infty$ . Again, the mixed-force value, even with  $n = 20$ , is the same, within the statistical error, as that of the converged trajectory. This indicates that dynamical and kinetic magnitudes, as well as structural or thermodynamic averages, are well reproduced even with quite large values of the boost factor  $n$ .

In conclusion, we have presented a method to greatly accelerate *ab initio* molecular dynamics simulations by combining cheap force evaluations with accurate converged ones. Our results show that the method is very robust with respect to the reduced accuracy of the cheap forces. Although the acceleration factor will undoubtedly depend on the system simulated, our present results indicate that factors of 10 can be expected in most cases.

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