

“Learn on the Fly”: A Hybrid Classical and Quantum-Mechanical Molecular Dynamics Simulation

Gabor Csányi,¹ T. Albaret,³ M. C. Payne,¹ and A. De Vita^{2,3}

¹*Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom*

²*Physics Department, King's College London, Strand, London WC2R 2LS, United Kingdom*

³*INFN-DEMOCRITOS National Simulation Center and Center of Excellence for Nanostructured Materials (CENMAT), University of Trieste, Trieste, Italy*

(Received 18 May 2004; published 19 October 2004)

We describe and test a novel molecular dynamics method which combines quantum-mechanical embedding and classical force model optimization into a unified scheme free of the boundary region, and the transferability problems which these techniques, taken separately, involve. The scheme is based on the idea of augmenting a unique, simple parametrized force model by incorporating in it, at run time, the quantum-mechanical information necessary to ensure accurate trajectories. The scheme is tested on a number of silicon systems composed of up to $\sim 200\,000$ atoms.

DOI: 10.1103/PhysRevLett.93.175503

PACS numbers: 62.20.Mk, 02.70.Ns, 31.15.Qg, 71.15.Pd

Many processes in materials involve strongly coupled subregions of the system which are best modeled in a “multiscale” fashion, i.e., by the concurrent use of different levels of description. As an example, the mechanical failure of brittle solids involves complex bond breaking processes at the advancing crack tip as well as chemically simpler stress concentration phenomena in a much larger region surrounding the tip [1,2]. Using a unique model, e.g., a quantum-mechanical Hamiltonian or a classical force field, in this or a similar situation is not a viable strategy. On the one hand, performing expensive quantum calculations on the whole system can rarely be afforded, as the system sizes and simulation times treatable in this way are severely limited. Even when possible, such calculations imply a significant waste of resources, since a simple classical interatomic potential would be sufficient to model most of the system. On the other hand, no classical potential can be used as the only tool to model the entire system unless it can be made accurate enough to describe the whole range of expected chemical reactions. Much effort has recently been devoted in this direction to develop “reactive” classical force fields capable of high accuracy for some specific materials and classes of reactions [3–6]. However, it is clear that considerable effort and subtlety are involved in adapting an existing potential [7] or developing a new one each time a new chemical situation is targeted. Indeed, the lack of straightforward transferability is the main disadvantage of the specialized classical potentials techniques, in striking contrast with the application of first principles techniques, which are computationally intensive but accurate and general. To date, developing a general analytic interatomic potential which is *a priori* capable of chemical accuracy in all situations still seems an overwhelmingly difficult task [7].

As a result, the use of multiscale modeling appears to be necessary to approach the crack (propagation) problem mentioned above and many others. Consequently, multi-Hamiltonian schemes have been proposed, which divide

the system into a “quantum” region where the more important chemical processes occur and a larger “embedding” region described by a less computationally intensive model. Matching these different regions mechanically [2,8–10] and chemically [11,12] is, however, a delicate issue. Perhaps the main practical drawback of these embedding approaches is that dedicated techniques have to be developed and judicious choices made [13] to represent the boundaries between regions.

In the present work, we retain the idea that a unique, classical force model should be used to describe the entire system to avoid boundary problems. Also, we aim at constructing a scheme which can be relied upon to be fully transferable, or in all cases no less transferable than some reference quantum model taken, such as an *ab initio* density functional theory (DFT) scheme. Moreover, we wish to be able to enforce the high accuracy of our reference quantum model where and when we choose to, across the system and during its time evolution. However, we take the view that no feasible analytic form for the classical force model can reproduce simultaneously the reference model’s accuracy (say, over a small domain of system configurations) and transferability (to all other such domains), since these two properties pose opposite requirements on the force model’s complexity (measured, for example, by the number of fitting parameters). We note that underlying this difficulty is a general problem of fitting techniques involving parameter optimization, where functional complexity has to be tuned as a compromise between bias and variance of the fit [14]. We thus renounce any attempt to develop sophisticated parametrized functional forms with sets of fixed-valued optimized parameters. Rather, we select a simple parametrized potential and “augment” it at run time with the necessary extra information, which is computed “on the fly” by means of accessory quantum calculations. These more expensive quantum calculations are the price we pay to ensure both the transferability and accuracy of

electronic-structure calculation in a simple and flexible scheme, which is well suited to investigate a range of multiscale processes. These ideas were outlined in [15].

We start by assuming the existence of a parametrized classical potential which captures the general physics of the system studied reasonably well [7,16]. We allow the parameters of the potential to take different values across the system, e.g., with independent parameters α_{ij} for each two-body term $V_2(\alpha_{ij}, R_i, R_j)$ corresponding to the pair of atoms i and j . The original potential is assumed to accurately describe only processes that are simple from a chemical point of view, but may be taking place throughout the entire system at all times, such as the elastic deformations of the atomic lattice far from an opening crack. We then set out to extend the applicability of the potential to the remaining, more complex processes such as the breaking and forming of chemical bonds which occur during the evolution of the system. The information “missing” from the classical potential is computed using “black box” engines [based, e.g., on a DFT or a tight binding (TB) formalism] and then incorporated “on the fly” into the potential by allowing an appropriate subset of its parameters to vary suitably with time.

A possible flow structure for the “learn on the fly” (LOTF) hybrid scheme using a force fitting [17,18] predictor-corrector approach is as follows: (1) *Initialization*: start with the physical system in its initial conditions, and with a reasonable choice of initial parameters for the classical potential. (2) *Extrapolation*: as in standard molecular dynamics (MD), use the potential with fixed parameters to generate a small number of time steps of the system trajectory. (3) *Testing*: in the latest configuration, the local validity of the classical potential is assessed on a site by site basis, and a selected subset of atoms is flagged for quantum treatment. (4) *Quantum calculations*: use any method which provides the desired accuracy to compute the forces on *only* the selected subset of atoms. (5) *Force fitting*: tune the parameters of the classical potential until they reproduce the accurate forces. (6) *Interpolation*: return the state of the system to that before the extrapolation and rerun the dynamics, interpolating the potential parameters between the old and the new values. (7) *Return to 2*.

As an example, we consider the diffusion of a vacancy in silicon. The empirical potential used is the Stillinger-Weber (SW) potential [16]:

$$E = \sum_i^N \left[\sum_{j \in (i,j)} \epsilon_1 (B_{ij}/r_{ij}^p - A_{ij}) f_{\text{cut}}(r_{ij}) + \sum_{j,k \in (i,j,k)} \epsilon_2 (\cos(\theta_{ijk}) - C_{ijk})^2 f_{\text{cut}}(r_{ij}, r_{ik}) \right], \quad (1)$$

where the first sum is over the atoms; the second and third sums are over pairs and triplets of atoms which include atom i . The cutoff functions f_{cut} go to zero exponentially when the interatomic distance reaches a chosen cutoff

value (3.77 Å). The parameters A_{ij} , B_{ij} , and C_{ijk} are allowed to vary with time. After initialization, in step (2) we extrapolate the dynamics at finite temperature for five MD steps, using the velocity Verlet algorithm with 1 fs time step. In step (3) we choose to compute accurate (TB) quantum-mechanical forces for the atoms located within 7.5 Å of the diffusing defect. A simple way to calculate these forces is to first construct for each atom a cluster including all its neighbors up to some given cluster radius, here set to 7 Å. To chemically terminate the cluster, the Si atoms bound to cluster atoms and located outside the cluster radius are replaced by hydrogen atoms. These are positioned along the direction of each substituted Si-Si bond at the Si-H equilibrium distance from the cluster atoms. The Hellman-Feynman force on the required atom is then computed after direct diagonalization of the cluster system. The forces on the central atom of each cluster (cf. Figure 1), are shown to converge quickly with cluster radius and to be relatively insensitive to the precise termination strategy [19]. We note that since only these forces are kept from the TB calculations, this implies that the system trajectory will not be affected by fine details in representing the boundary. In step (4) the parameters of the classical potential are optimized by minimizing the squared difference between forces given by the classical model and the accurate forces. For atoms that do not have a quantum-mechanical force calculated on them, the current classical force is used as the target of the optimization. Tests show that local parameters related to atoms which are further than a few neighbor shells outside the QM region do not change appreciably with the fit. The optimization [step (5)] is therefore limited to the two-body and three-body terms of the potential (1) involving atoms in a spherical region of 12 Å radius centered on the diffusing defect. About 30 conjugate gradient steps in parameter space are sufficient to perform a converged fit, the maximum residual deviation from the target forces being typically less than 0.01 eV/Å. The LOTF value for the Si vacancy diffusivity [20] obtained from a 1 ns constant temperature (CT) simulation using the above scheme at $T = 1400$ K with a 215 atom periodic system is $(2.1 \pm 0.4) \times 10^{-6}$ cm²/s [19]. This compares well with the value calculated using the TB scheme of $(2.3 \pm 0.2) \times 10^{-6}$ cm²/s, obtained using the model in [21] [the Stillinger-Weber potential gives $(3.4 \pm 1.0) \times 10^{-5}$ cm²/s]. We report in Fig. 2 results for the vacancy diffusivity in Si as a function of temperature, obtained by

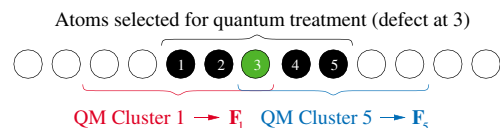


FIG. 1 (color). Schematic of the QM zone centered on the defect in position 3, and of two of the clusters used by the QM “black box” to compute the forces used in the fit (see text).

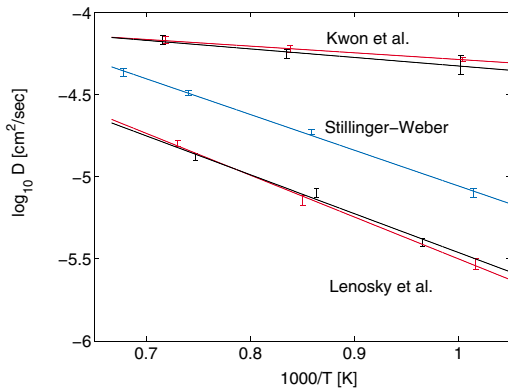


FIG. 2 (color). Arrhenius plot of the silicon vacancy diffusivity obtained by the present scheme fitted “on the fly” on different TB models (red), compared with the results of fully TB simulations (black) and fixed-parameter SW potential (blue).

CT simulations using the fixed-parameter SW potential, two different TB schemes [22,23], and our hybrid scheme. To be able to perform several fully quantum-mechanical simulations we used a 64 Si atom cubic cell. As the cell is so small, here we compute the exact TB forces to be used in the LOTF fit by direct diagonalization of the periodic system Hamiltonian. We note that the large difference between the results obtained by fitting the scheme on the two different quantum models is due to the different predictions of these models in accurate quantitative computations, reproduced by the present method. This emphasizes the fact that the present scheme can at best be expected to reproduce the results of the QM model that it is given [24], but can in no way improve its accuracy.

To further elucidate how the scheme adapts to the local environment, we report in Fig. 3 the time evolution of the parameters C_{ijk} at a dimerized Si[100] surface at room temperature. In the bulk these angle parameters remain at all times close to their $-1/3$ equilibrium value (left). However, on the reconstructed surface, the equilibrium angle on the lower side of the buckled dimers (inset) is lowered to almost 90° . The corresponding parameters “learn” this by switching to a value close to zero, and flip back and forth between zero and $-1/3$ as the buckling direction varies with time (right).

Moving to a problem where a fully quantum approach would be practically unfeasible, we simulate the gliding motion at 900 K of an opposing pair of 30° partial dislocations in Si, using a 4536 atom unit cell. We flag for QM treatment all atoms within 7.0 \AA of the dangling bonds (undercoordinated atoms) formed during dislocation motion, corresponding to two disjoint QM regions of 100–120 atoms, which follow the diffusing kink of each partial dislocation. On a single 1200 MHz Pentium III processor, the hybrid simulation takes $\sim 3\text{--}4$ CPU minutes per MD step using a cluster radius of 7 \AA . For comparison, a MD step takes 11 h using a state-of-the-art linear scaling tight binding code [25], while a conventional

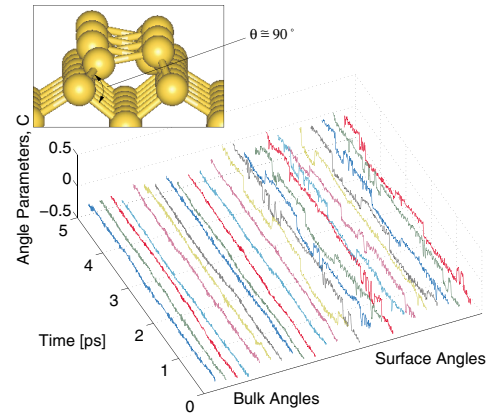


FIG. 3 (color). Time evolution of angle parameters near a Si[100] reconstructed surface. A representative “surface angle” is marked in the inset with a black arc. The “bulk angle parameters” are all for angles centered on atoms of the third atomic layer.

direct diagonalization would be approximately an order of magnitude slower. Improving on the accuracy of the classical potentials is crucial to simulate this extended defect. LOTF simulations on this system reveal a bond topology for the free energy minimum at 900 K which differs from that obtained in the same conditions (and at 0 K [26]) from the SW model, with a square of atoms formed adjacent to an antiphase defect (red atom in Fig. 4), and a different defect migration pathway. While the TB model used [23] may still not capture every relevant feature of the phenomenon under study, these results indicate the need to enforce electronic-structure precision. Indeed, in dislocation dynamics the inaccurate canonical phase space sampling provided by classical potentials is regarded as the main source of discrepancy between theory and experiment [26].

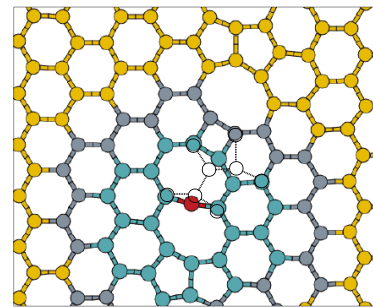


FIG. 4 (color). Equilibrium structure of the Si 30° partial dislocation left kink from a 900 K hybrid simulation (only the glide plane atoms are shown). One undercoordinated atom (red) and its neighbors (blue) are flagged for QM treatment. The gray atoms further away complete the set of atoms for which potential optimization is performed. The parameters corresponding to interactions between the yellow atoms in the external region are not updated. Empty circles represent the stable 0 K structure [26].

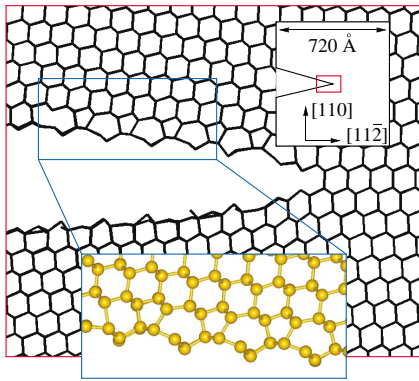


FIG. 5 (color). Propagation of the $(111)[\bar{1}\bar{1}0]$ crack in silicon, using the LOTF scheme and the SIESTA code as quantum engine. Brittle fracture propagation on a (111) cleavage plane is correctly predicted. Note the 2×1 Pandey reconstruction just appearing on the upper opening surface.

We next test the scheme on a much larger system containing approximately 200 000 atoms, to simulate brittle failure in silicon under uniaxial tensile stress. About 300 atoms near the crack tip are treated quantum mechanically using the SIESTA DFT package [27] as the QM black box. A 2 ps simulation (2000 MD time steps) took 26 h on a 32-processor IBM SP-SMP computer, a single cluster calculation taking about 1 CPU minute. While the full scientific results, obtained using both TB [28] and DFT [27] black boxes, will be presented elsewhere, we note that the fixed-parameter SW model incorrectly predicts tip blunting and amorphization [2,29]. The incorporation of quantum-mechanical information using the LOTF scheme, however, recovers the correct brittle behavior, consistent with the QM/MM (quantum mechanics/molecular mechanics) results of [29]. The 2×1 reconstruction of the crack surface (not predicted by the TB model) is also reproduced using the first principles black box (Fig. 5). Longer simulations allow the investigation of even subtler effects such as the anisotropy of propagation direction in the Si(110)[010] crack system [30].

In summary, we proposed and tested a hybrid molecular dynamics scheme in which the accuracy can be systematically monitored and improved and which does not suffer from boundary problems. The embedded quantum region can be treated by a number of methods in a “black box” fashion, which can be easily used concurrently and matched through the unique, general interface provided by the fitting procedure. So far we have implemented interfaces for the DFTB [31], SIESTA [27], and FIREBALL [32] packages, besides several empirical TB schemes.

The authors are indebted to Arthur Voter and Furio Ercolessi for carefully reading the manuscript, and acknowledge funding from the EPSRC Grant No. GR/S61263/01 and EU Grant No. HPRN-CT-2000-0154. We

thank Stefan Goedecker for providing the code that was used to benchmark the linear scaling tight binding method.

-
- [1] S. Kohlhoff *et al.*, *Philos. Mag. A* **64**, 851 (1991).
 - [2] F.F. Abraham *et al.*, *MRS Bull.* **25**, 27 (2000).
 - [3] A.C.T. van Duin *et al.*, *J. Phys. Chem. A* **105**, 9396 (2001).
 - [4] S.J. Stuart *et al.*, *J. Chem. Phys.* **112**, 6472 (2000).
 - [5] A.P. Horsfield *et al.*, *Phys. Rev. B* **53**, 12694 (1996).
 - [6] D.G. Pettifor *et al.*, *Comput. Mater. Sci.* **23**, 33 (2002).
 - [7] D.W. Brenner, *Phys. Status Solidi B* **217**, 23 (2000).
 - [8] E.B. Tadmor *et al.*, *Philos. Mag. A* **73**, 1529 (1996).
 - [9] V.B. Shenoy *et al.*, *Phys. Rev. Lett.* **80**, 742 (1998).
 - [10] G.S. Smith *et al.*, *Phys. Rev. Lett.* **84**, 1260 (2000).
 - [11] J. Gao, *Rev. Comput. Chem.* **7**, 119 (1995).
 - [12] N. Reuter *et al.*, *J. Phys. Chem. A* **104**, 1720 (2000).
 - [13] A. Laio *et al.*, *J. Chem. Phys.* **116**, 6941 (2002).
 - [14] C.M. Bishop, *Neural Networks for Pattern Recognition* (Oxford University Press, Oxford, 1995).
 - [15] A. DeVita and R. Car, *Mater. Res. Soc. Symp. Proc.* **491**, 473 (1998).
 - [16] F. Stillinger and T. Weber, *Phys. Rev. B* **31**, 5262 (1985).
 - [17] F. Ercolessi and J.B. Adams, *Europhys. Lett.* **26**, 583 (1994).
 - [18] A. Laio *et al.*, *Science* **287**, 1027 (2000).
 - [19] A 7.0 Å cluster radius is, e.g., sufficient to ensure in the whole QM zone a <0.1 eV/Å rms deviation from the exact TB forces in a 0.5 ps LOTF simulation of a vacancy diffusion event in a 215 Si atom system at 1400 K. Constructing clusters of similar size including all Si atoms up to a chosen neighbor shell rather than up to a fixed radius yields analogous results. We note that for the purposes of this study we restrict ourselves to systems where long range forces do not appear.
 - [20] M. Tang *et al.*, *Phys. Rev. B* **55**, 14279 (1997).
 - [21] D.R. Bowler *et al.*, *J. Phys. Condens. Matter* **10**, 3719 (1998).
 - [22] I. Kwon *et al.*, *Phys. Rev. B* **49**, 7242 (1994).
 - [23] T.J. Lenosky *et al.*, *Phys. Rev. B* **55**, 1528 (1997).
 - [24] We obtained analogous results for the diffusion of the Si self-interstitial, for which the SW potential fails to predict the correct 0 K structure.
 - [25] S. Goedecker, *Rev. Mod. Phys.* **71**, 1085 (1999).
 - [26] V.V. Bulatov *et al.*, *Philos. Mag. A* **81**, 1257 (2001).
 - [27] D. Sanchez-Portal *et al.*, *Int. J. Quantum Chem.* **65**, 453 (1997).
 - [28] G. Panzarini and L. Colombo, *Phys. Rev. Lett.* **73**, 1636 (1994).
 - [29] N. Bernstein and D.W. Hess, *Phys. Rev. Lett.* **91**, 025501 (2003).
 - [30] R. Pérez and P. Gumbsch, *Phys. Rev. Lett.* **84**, 5347 (2000).
 - [31] Th. Frauenheim *et al.*, *Phys. Status Solidi B* **217**, 41 (2000).
 - [32] J.P. Lewis *et al.*, *Phys. Rev. B* **64**, 195103 (2001).