Combining Tight-binding and Molecular dynamics Methods to Model the Behaviour of Metals in the Plastic Regime

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Abstract

Ultra-precision machining of metals, the breaking of nanowires under tensile stress and fracture of nanoscale materials are examples of technologically important processes which are both extremely difficult and costly to investigate experimentally. We describe a multiscale method for the simulation of such systems in which the energetically active region is modelled using a robust tight-binding scheme developed at the Naval Research Laboratory (NRL-TB) and the rest of the system is treated with molecular dynamics. We present a computer code implementing the method, geared towards non-equilibrium, cross-scaled tight-binding and molecular dynamics simulations. Apart from the presentation of the method and implementation, we discuss preliminary physical results obtained and discuss their validity.

1 Introduction

Ultraprecision machining, or UPM, is a process in which a hard (usually diamond or CBN) tool machines away a layer of workmaterial as thin as a few nanometers. The machined materials include soft metals, such as aluminum or copper, glasses and semiconductors. A prime example of a technologically important application of UPM is the finishing of aluminum platters for magnetic hard disk drives [1], [2]. Experimental analysis of UPM is both extremely difficult and costly to investigate: the need to damp vibrations, assuring adequate vacuum and the necessity to use AFM or STM to visualize the results being the most important obstacles.

High costs of experimental setups have led researchers to explore the possibilities of computer simulation of ultraprecision machining processes. Molecular dynamics (MD) is the traditional method of choice because of its relative simplicity and good scalability. The increase of available computational power offers today the opportunity to perform MD simulations of UPM using $10^4$-$10^5$ atoms with timescales in the order of a few nanoseconds [1], [2], [3].

Such simulations are performed in the non-equilibrium (NEMD) regime, with the tool atoms usually having their velocity reset to a constant value at each step. The workmaterial needs artificial “clamping” to ensure it remains in place and does not translate upon contact with the tool. Periodic boundary conditions may [3] or may not [1] be used along the direction perpendicular to that of the machining. The potentials used are either pairwise, such as Morse potential [2] or many-body, such as the Sutton-Chen potential [3]. Since these are parametrized to reproduce the behaviour of atoms close to their equilibrium positions, they are rather unreliable in situations where bonds are ruptured and such is the case in the part of the system where the tool tip enters the material. In fact it was shown that for brittle fracture of silicon the widely used Stillinger-Weber MD potential gives incorrect predictions, as compared to DFT-based methods [6].

Apart from UPM there are other interesting systems and processes which also do not lend themselves easily to experimental investigation and contain regions where bond-breaking takes place, which renders MD simulations thereof unreliable. Among these are: metallic nanowires breaking under stress, nanoindentation, nano-scratching, fracture of nanoscale materials. If the system is small (less than $10^3$ atoms) quantum-based methods, such as DFT or tight-binding (TB) which deal with the electronic structure explicitly may be used. For larger systems the computational cost of these methods quickly becomes prohibitive. There is, however, a great need for methods that would allow for the treatment of such systems, thus allowing to simulate more complex materials, auxetics being one of the greatest challenges.

One solution of this problem is offered by the so-called cross-scaling methods, in which a part of the system that needs quantum-based treatment is identified and treated accordingly, while the remaining part of the system is simulated using the MD method. This approach attempts to benefit from the advantages of both methods, however it suffers from its own problems, such as difficulty in determining the position of the region and dealing with boundaries between the two partitions of the system. Handshaking the two methodologies is the most enduring task.
The paper is organized as follows. In section 2 we describe the formulation of the tight-binding method and the molecular dynamics method, later focusing on bridging of the two methods. Our computer code implementing the cross-scaling is then characterized, along with the simulation procedure. In section 3 we present results of preliminary tests used to validate the method. Section 4 contains conclusions and final remarks.

2 Computational method

2.1 The NRL-TB method

Tight-binding is the only quantum-based method that allows for the treatment of systems comprising several hundred atoms on a typical workstation. While relatively simple compared to DFT-based methods, it still captures the relevant electronic effects, at least in a qualitative manner. The method reduces the Schrödinger equation to a generalized eigenvalue problem by expanding one-electron wavefunctions as linear combinations of atomic orbitals. Following Slater and Koster [7] matrix elements of the Hamiltonian are separated into an angular-dependent part and distance-dependent two-center integrals, which are then parametrized. Brute-force matrix diagonalization which is involved in solving the eigenvalue problem scales as $O(N^3)$ and is usually the bottleneck of the calculations. $O(N)$-scaling methods have also been developed, but since they rely on bond locality, they are less transferable and perform poorly for metals [8]. In the tight-binding formalism the energy of the system is written as:

$$E_{TB} = 2 \sum_{n}^{N_{occ}} \varepsilon_n + F[n(r)],$$

(1)

where the first term, involving summation of the electronic eigenvalues $\{\varepsilon_n\}$ over all occupied levels is the band structure energy. The second term is an unknown functional of the charge density $n(r)$ and accounts for the remaining density-functional energy (coulombic core-core repulsion, canceling out the double counting of electron-electron interactions, etc.) This second term is usually approximated by a parametrized repulsive pair potential, which necessitates using extra parameters apart from the ones describing the two-center integrals.

In the Naval Research Laboratory tight-binding (NRL-TB) total-energy method [9]-[23], developed by Mehl and Papaconstantopoulos the second term is rid of by clever shifting of the underlying DF Kohn-Sham potential. This narrows down the parameter space at the price of introducing a dependence of the on-site matrix elements on the local environment. It can be shown [9]-[11] that such approach is well-justified and is a generalization of the pair potential typically used for $F[n(r)]$. The NRL-TB method offers transferability superior to other TB variants and parameter sets for many d-metals are readily available. These advantages have made it our method of choice for the quantum-based region of the system, despite the fact that the computer code implementing the method is no longer given away by the authors.

2.2 The molecular dynamics method

In the MD method a system of classical particles interacting with one another via an empirical potential is followed in discrete timesteps. Analytical differentiation of the potential yields forces acting on the particles and numerical integration of Newtonian equations of motion gives positions of the particles in subsequent timesteps. Aided with the link-cell method, it scales as $O(N)$ and simulations of hundreds of thousands of particles for timescales of a few nanoseconds are feasible on a typical workstation. A usual timestep is in the order of 1 fs, we have chosen $\Delta t = 2.5$ fs. We have decided to choose a fourth-order Gear predictor-corrector algorithm as the numerical integrator.

2.3 nanoTB code

After careful investigation of available non-commercial MD codes we have decided that none of them met our needs for simulating ultraprecision machining or other systems involving plastically deforming metals. However a parallel code suitable for performing NEMD simulations was being developed in our group as part of research on carbon nanotubes [4]. This code was easily adapted to our task of interest by the introduction of the Sutton-Chen many-body potential. The nanoMD program implements the molecular dynamics method and is geared towards simulations involving external forces, therefore making it easy to fix atoms in position, apply constant translatory or rotational forces, etc. A selection of potentials, including Morse, Sutton-Chen, Brenner, Finnis-Sinclair, harmonic and anharmonic is available. Nosé, Nosé-Hoover and gaussian thermostats have also been implemented. It has been used with success for the MD simulation of UPM [3].

To perform cross-scaling simulations we have implemented the NRL-TB method from scratch, incorporating it into our code. The program, now called nanoTB, accepts the TB parameter files available from the NRL website. Two modes of operation are possible – in the first a TBMD simulation is performed, that is the whole system is treated with the TB method, and the quantum-based forces it supplies drive the MD simulation. The second mode allows for a cross-scaling TB+MD simulation – regions of the system are designated for which a TB calculation takes place, in these regions the quantum-based forces replace the forces obtained from MD, while
the rest of the system is treated with MD. Forces are obtained from the TB hamiltonian matrix element derivatives by means of Hellmann-Feynman theorem. Each region may take a spherical, cylindrical or cuboid shape and be either fixed in size or dynamically adjust to accommodate a fixed number of atoms. For the cuboid and cylindrical region shapes periodic or fixed boundary may be used. Charge self-consistency may be achieved by means of Hubbard-U method or be neglected. Fermi broadening of energy levels is used. The regions may be fixed in place, move with uniform velocity (e.g. along with the tool tip) or be made to follow energy peaks in the system (useful for tracing defects).

2.4 Handshaking TB and MD

Devising a physically sound method for embedding the ab-initio region within an MD system is of utmost concern for cross-scaling simulations. Spurious effects resulting from the cessation of bonds at the TB/MD interface as the TB region is isolated from the rest of the system have plagued cross-scaling simulations from their inception [5], [26], [27]. The approach usually taken to account for the unsaturated valencies is to surround the quantum region with virtual atoms, usually monovalent, which serve to terminate the dangling bonds [5], [27]. Since they introduce extra atoms into the calculation, these link-atom methods (LAM) increase the computational load and require a parametrization of the method not only for the species of interest but also for the interactions between it and the link-atoms. Even more important is the fact that they rely on bond locality which prohibits their use for metallic systems. In fact it seems that no handshaking method that could deal with delocalized bonding has ever been proposed.

Our first attempt to approach this problem was as follows. We have conceded to the fact that unterminated valencies will be present in the TB region but have instead concentrated on reducing their influence on the atomic trajectories. Assuming that the greatest disturbances in the TB-generated forces would be present in the outer part of the quantum region, we decide to give more credence to the MD forces for the atoms close to the region perimeter. This was achieved by taking for the force acting on atom \(i\) within the region a weighted average of the TB force and the MD force, the weight being the relative distance \(d\) of the atom from the region centre:

\[
\vec{F}_i = d \cdot \vec{F}_i^{MD} + (1-d) \vec{F}_i^{TB}.
\]  

This procedure was meant to result in a gradual switching from the TB forces to the MD forces as the former became more unreliable.

Unfortunately this simple approach has led to serious unphysicalities in the test cases we have studied. Upon centering a spherical TB region of 14 Å in diameter on a self-interstitial defect in Cu, the quantum-based forces acting on the atoms close to the perimeter of the region were two to three orders of magnitude greater than the corresponding MD forces. This was due to the fact that these atoms were only very slightly disturbed from their lattice positions, yet they were heavily influenced by the isolation of the TB region from the rest of the system. As a consequence, even with \(d = 0.95\) the force computed from (2) was overestimated by an order of magnitude or so for all atoms close to the region boundary. A similar scenario occurred for a cylindrical region centered on one of the edges of a cuboid of 1638 copper atoms, mimicking a workmaterial to be machined. The strong TB forces resulting from the isolation of the region easily outweighed the relatively small MD forces acting on these same atoms. As the hamiltonian resulting from (2) is not conservative, this resulted in constant increase of system energy, effectively melting the surrounding material.

Thus it became obvious that a more sophisticated method of combining the TB and MD forces was needed. We have settled for a method similar in concept to the one described, but using a more aggressive mixing in of the MD forces. We have decided to cut-off the influence of the TB forces using a smooth function similar to the cutoff function used in the NRL-TB method [12]. Instead of (2) we use

\[
\vec{F}_i = w(d) \vec{F}_i^{MD} + w(1-d) \vec{F}_i^{TB},
\]  

where

\[
w(d) = \frac{1}{1 + \exp\left(-\frac{d-l}{5}\right)}.
\]

with \(l = 0.06\). This leads to a non-linear weighing of the TB and MD forces.

![Fig. 1: The shape of the weighing function \(w(d)\).](image)

Note \(w(0) \approx 0, w(1) \approx 1\).

This improved embedding has proven more successful against our test cases. As an example consider a cylindrical quantum region of diameter 13.25 Å placed on a surface of a cuboid, with the cylinder
axis parallel to the cuboid edge. This system consisting of 4305 total atoms and 120 TB atoms was simulated for 8 ps and results of the two mixing methods were compared.

The artifacts introduced by the nonlinear method were markedly smaller, although still visibly present. This, naturally, comes at the cost of having to extend the region in practical applications as the atoms further than \( d = 0.5 \) from the region centre are effectively driven by the MD method, however their inclusion in the TB calculation serves to create a proper local quantum environment for the atoms closer to the region centre.

### 2.5 Simulation procedure

As a preliminary test of our code and the nonlinear mixing method, we have performed a cross-scaled simulation of nanoscratching of a copper workmaterial with a copper tool. The workmaterial was a cuboid of 20x10x5 fcc unit cells, for a total of 4305 atoms. The tool consisted of a cuboid of 8x8x5 fcc unit cells (1445 atoms), rotated by 45 degrees along the \( z \) axis and moving along the [0 1 0] direction. Periodic boundary conditions were used along the \( z \) (in-plane) direction. Atoms on the bottom surface of the workmaterial were fixed to prevent it from translating upon contact with the tool. For simplicity the tool was assumed to be infinitely hard (all forces acting upon it were ignored.) the tool moved with a uniform velocity of 10 m/s, which is considerably more realistic than in other simulations of UPM [1], [2]. A pure MD simulation using the Sutton-Chen potential was performed for comparison. The quantum region was cylindrical with periodic boundary conditions along the \( z \) axis and was centered on the tool tip, moving with the same velocity as the tool. It was taken to be only 8 Å in diameter for efficiency reasons, in realistic simulations the region should have a radius of at least 6.62 Å, since this is the cut-off distance for Cu in the NRL-TB method. Since the region was fixed in size, the number of atoms contained within it varied with time, with an average of 70 atoms. The simulations were performed at 300 K with a Nosé-Hoover thermostat having a time constant of 250 fs. A timestep of 2.5 fs was used. Initially the tool tip was at a distance of 4.75 Å from the workmaterial, giving it ample time to equilibrate before contact was made.

### 3 Results and discussion

We consider the presented simulation to be merely a preliminary test, therefore we look at the obtained results only qualitatively. The differences between the cross-scaled and the reference, pure MD simulation are rather subtle, but noticeable. For both simulations we observe the jump-to-contact (JC) phenomenon when the distance between the tool tip and the workmaterial is about 4 Å. This is in agreement with pure MD simulations described in [1], [24], [25]. Since the tool is infinitely rigid, it is the workmaterial that deforms slightly to contact the tool. At this point the cross-scaling and the reference simulation are expected to perform identically, because as the TB region is centered on the tool tip, at this distance there are only 15 workmaterial atoms within the region and these are driven almost exclusively by MD.
Until the distance between the tool tip and the workmaterial reaches about 1.5 Å, the values for the normal force acting on the tool are practically identical in the two simulations and extremely small – the tool is attracted by the workmaterial with a force lower than 0.1 nN. This force fluctuates quasi-periodically as the workmaterial "wiggles" under the tool in response to the attraction. As the tool tip gets closer than 1.5 Å to the surface, the force becomes repelling and then rises steadily after contact as the tool penetrates the workmaterial. The forces achieve their highest value of about 0.8 nN at the penetration depth of 8 Å (where the simulation terminates). During the course of the simulation, as more atoms are treated with TB, the differences between the simulations become noticeable. The normal forces observed in the cross-scaling simulation are seen to be 10-30% greater than the corresponding pure MD forces.

Taking a closer look at the configuration of the system after the tool has entered the workmaterial 5.25 Å deep, we note slight differences between the cross-scaling and reference simulation. A comparison of the figures below reveals that the cross-scaled simulation shows a smaller disturbance of workmaterial several layers under the tool tip. Slight differences in the pressure maps (Fig. 5) and the fact that the normal force experienced by the tool is greater for the cross-scaling simulation lead to a supposition that the material is in fact slightly harder than pure MD simulations would predict.

4 Conclusion

We have developed a computer code that allows for cross-scaling simulations using the methods of NRL total energy tight-binding and molecular dynamics.
in combination. The program allows for the embedding in an NEMD simulation a number of quantum-based regions that are dynamic in size and position and may take various shapes. We have considered two methods that would tentatively deal with the problem of untermined valencies in metallic systems on the TB/MD boundary, showing the first one to fail and the second to be moderately successful. The nonlinear mixing method minimizes the surface effects on region boundaries at the price of having to extend the region, which increases the computational load. Also the hamiltonian resulting from the application of the method is not conservative. We have tested the code and the nonlinear cross-scaling method on several simple systems, finding the code to work and the method to behave better than the linear one we have proposed earlier. For the simulation of nanoscratching, our cross-scaling method gave similar, but not identical results to the pure MD simulation, we bear in mind, however, that the region size used for the test was too small for practical applications. We envisage adapting the recent learn-on-the-fly method [28] to the Sutton-Chen potential in order to attack the problem of embedding quantum-based calculations within an MD framework from a different perspective.

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