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# DFT Embedding and Coarse Graining Techniques

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Classical molecular dynamics and first principles quantum mechanical calculations are two of the most important methods currently used to model physical systems at the atomic level. The former allow simulations of millions of atoms to be carried out on a nanosecond timescale but the accuracy is limited by the requirement to use simple parameterisations as interatomic potentials. If the scientific question of interest can be effectively answered by considering the behaviour of a very small number of atoms, up to around a hundred, then *ab initio* approaches allow this limitation to be overcome. In many cases we can extract enough information from these accurate quantum mechanical calculations to parameterise less transferable, but far less expensive, models and use them on a larger length scale. For some systems however, it is impossible to separate the behaviour on the various length scales, since the coupling between them is strong and bidirectional. Then the only option is to carry out a *hybrid* simulation, where some parts of the system are treated at a higher level of accuracy; this is the subject of this lecture.

## 1 Introduction

Over the last twenty years, the *ab initio* methods described in the previous lectures have made modelling of simple systems reliable, accurate and routine. This is partly due to the significant increase in capacity and speed of available computers and partly to the development of high quality codes that make effective use of these resources. As a result,

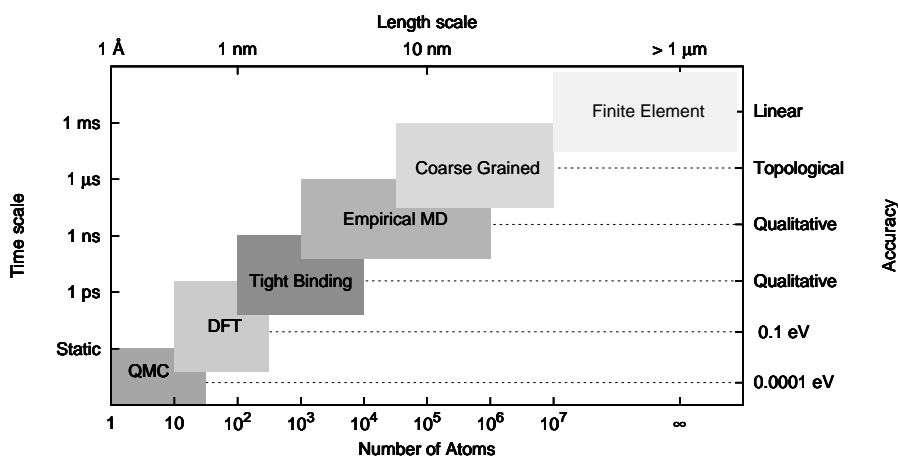


Figure 1. Schematic representation of the range of length- and time-scales accessible to a variety of modelling methods, from quantum Monte Carlo (QMC) for very accurate, very expensive static calculations through to approximate methods such as finite-element modelling.

attention is now focusing on modelling larger scale, more complex systems. Representative examples from fields as disparate as biology and materials science include enzyme catalysis<sup>1</sup> and defect migration in semiconductors. Ideally, we would simulate such systems using entirely first principles methods, free of empirical parameters and the accuracy and transferability problems associated with them. However, *ab initio* molecular dynamics is limited to simulating a few hundred atoms for up to a few picoseconds. Using more approximate methods (*e.g.* tight binding), the number of atoms can be extended to perhaps thousands, or the time period increased by a few orders of magnitude, but for many problems this is still insufficient. Fig. 1 illustrates the approximate range of application of various modelling techniques and makes clear the challenges we face if we wish to model complex problems with high accuracy.

### 1.1 Hierarchical Modelling

In recent years, there has been a great deal of work on multiscale methods that attempt to apply accurate quantum calculations to larger systems in one way or another. Most commonly, such methods are examples of *hierarchical multiscale modelling*, where the results of a calculation at one scale are used to parameterise less accurate calculations at a larger scale, making bigger systems or longer simulation times possible. There are many such examples of DFT based coarse graining in the literature including: using DFT forces to parameterise empirical interatomic potentials; calculating defect energies, often in different charge states, to their determine equilibrium concentrations; calculating surface stresses and the energies of surface steps to determine the thermodynamic properties of stepped surfaces.

For many materials and biological processes, the relevant timescale is of the order of milliseconds or longer, well beyond the capability of traditional molecular dynamics. To make progress we can either form a hierarchical multiscale model by coarse graining the system and considering the dynamics of the aggregate particles, or we can try to extract activation energies and reaction pathways from static calculations or short MD runs to parameterise Monte Carlo models. For a review of hierarchical multiscale methods and examples of their application, see Ref. 2.

### 1.2 Simultaneous Modelling

There is a large class of problems where the physical processes on the various length scales are strongly coupled and cannot be separated into a series of independent calculations; often this is because the nanoscale phenomena is driven by forces determined at least partially on the macroscopic scale. Simulation of such systems requires *simultaneous* coupling of length scales. Over the last ten years there has been much effort to devise schemes, referred to as *hybrid* or *embedded* methods, that combine a range of modelling techniques into a single simulation.

Occasionally, the large scale processes are so simple that they can be simulated very easily, as an example Martonak<sup>3</sup> added a classical pressure reservoir of soft spheres to an *ab initio* simulation of a small molecule. Usually, however, the large scale behaviour requires a more complex model to accurately capture the physics; this will be assumed to be the case for the remainder of the work discussed in the lecture.

### 1.3 Multiscale Applications in the Solid State

Stress induced defect processes in metals and semiconductors often give rise to strongly coupled multiscale phenomena. Examples include point-defect diffusion, dislocation motion, grain boundaries and, of course, the prototypical multiscale modelling problem: fracture.

*Point-Defect Diffusion* The stability and migration of point defects in semiconductors is affected both by local chemical interactions and long range strain fields. An example long range effect is the strain field resulting from the lattice mismatch between epitaxial layers in semiconductors. Although the quantum mechanical treatment of the bonding rearrangement around a defect requires only a few hundred atoms, we would need to include thousands more atoms to accurately represent the inhomogeneous strain environment, particularly if we are to model interactions between multiple defects.

*Dislocation Motion* The strength of many materials is dominated by the behaviour of their dislocations. The core of a dislocation is a 1D region in which the bonding is significantly distorted. Dislocations in covalent materials move by the formation of kinks in the dislocation, where the bonding is very highly distorted. As the kink moves, so does this region of distortion. This motion requires bond breaking and reformation, therefore this region should be modelled by a highly accurate quantum mechanical technique.

*Grain Boundaries* It is not always possible to assume perfect single crystal structure and ignore the effect of grain boundaries when studying the physical and electronic properties of semiconductors. This is true for many materials of growing technological relevance, for example gallium nitride, silicon carbide and diamond.<sup>4</sup> Grain boundaries change the crystal structure on two length scales: they introduce long-range elastic distortion and local bonding disorder. They also act as sinks and sources for dislocations and traps for dopants, electrons and holes, further increasing the local chemical complexity. A multiscale description is needed to describe these systems since empirical interatomic potentials describe the long range-interactions adequately but local rebonding requires quantum mechanical accuracy.

*Brittle Fracture* Fracture is perhaps the best example of a multiscale materials process. The conditions for crack propagation are created by stress concentration at the crack tip, and depend on macroscopic parameters such as the loading geometry and dimensions of the specimen.<sup>5-8</sup> In real materials, however, the detailed crack propagation dynamics, are entirely determined by atomic scale phenomena since brittle crack tips are atomically sharp and propagate by breaking bonds, one at a time, at each point along the crack front.<sup>9,10</sup> This means the tip region is primarily a one dimensional line, perpendicular to the direction of propagation, and so it should be possible to define a contiguous embedding region to be treated with a more accurate model in a hybrid simulation. There is a constant interplay between the length scales because the opening crack gives rise to a stress field with a singularity at the tip,<sup>11</sup> as illustrated in Fig. 2, and in turn it is this singular stress field which breaks the bonds that advance the crack. Only by including the tens of thousands of atoms that contribute significantly to the elastic relaxation of this stress field can we hope to accurately model the fracture system, and thus a multiscale approach is essential.

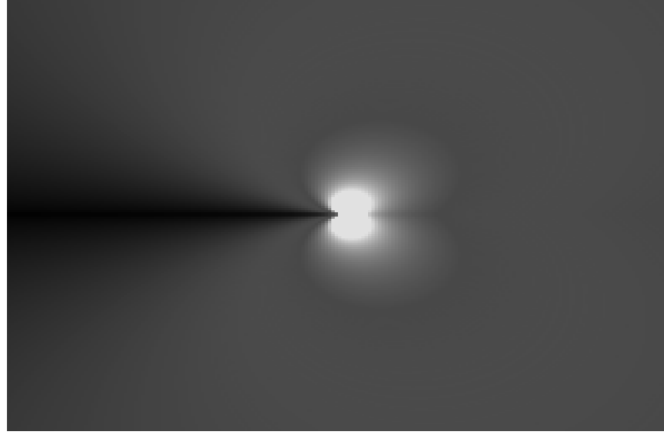


Figure 2. Maximum principal stress near the the tip of a crack under uniaxial tension in the opening mode, from the linear elastic solution. Light areas are the most highly stressed and dark the least.

Brittle fracture is the prototypical problem that has spurred many recent advances in the field of hybrid modelling of materials systems. For an example of a recent hybrid approach to modelling the fracture of silicon, see Ref. 12.

## 2 Coupling Continuum and Atomistic Systems

In the lecture, we shall concentrate on hybrid schemes which link quantum mechanical and classical modelling, but to provide some historical background, we shall first look briefly at a larger length scale. The pioneering hybrid simulations of materials systems were performed by Kohlhoff,<sup>13</sup> where classical atomistic and continuum elastic models were coupled to successfully model the directional cleavage anisotropy of a BCC crystal. This approach has been developed in the *quasicontinuum* (QC) method of Tadmor *et al.*<sup>14</sup>

The key problem with coupling atomistic and continuum models of matter is finding ways to connect these conceptually very different descriptions. Atomic positions need to be mapped onto a continuous displacement field, and energy calculations from interatomic potentials in the atomistic region and constitutive laws in the continuum region need to be harmonised. In the QC approach, a small subset of the atoms that would appear in a fully atomistic model are selected to represent the system as a whole, with a higher sampling density in highly deformed regions. The system is divided into cells, with one representative atom in each cell, as illustrated in Fig. 3. We assume that the energy of all the atoms in each cell is the same as that of the representative atom. The energies of these representative atoms are computed from the local environment, either from constitutive laws in areas that are nearly homogeneously deformed, or fully atomistically for non-uniformly deformed regions.

The atomistic and continuum methods are not completely compatible: non-physical forces arise on the continuum side of the boundary since it looks like an artificial surface.

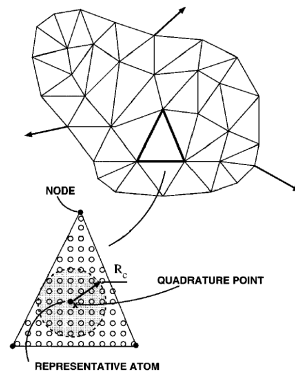


Figure 3. Schematic illustration of the finite element discretisation of a solid in the quasicontinuum method. The lower panel shows the representative atom for a particular triangular element. Reproduced from Ref. 14

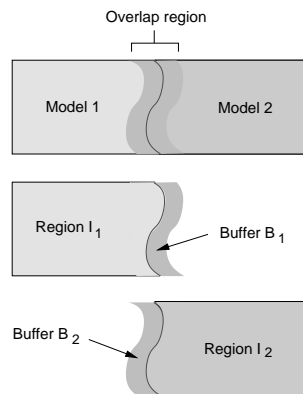


Figure 4. Schematic showing how overlap buffers can be used to solve the boundary problem in a classical/classical embedding scheme, where all interactions are short ranged.

The atomistic interactions used in QC are limited to be nearest neighbour models so there are no artificial forces in the atomistic region. In a refinement of the QC method, Shenoy *et al.*<sup>15</sup> removed these ghost forces in what they called the dead load approximation. The QC method has been applied to many systems, for example to study the interaction of dislocations with grain boundaries<sup>16</sup> and the effect of grain orientation on fracture.<sup>17</sup>

### 3 Coupling Two Classical Atomistic Systems

As a prelude to looking at the difficulties posed when attempting to couple quantum and classical systems, let's consider how two classical atomistic models could be combined. Providing the models are both short ranged, a straightforward treatment of the boundary is possible. We allow the regions to overlap as shown in Fig. 4, then evaluate the energy for the two regions separately, with a buffer region for both calculations. The locality of

the classical potentials means that each of these energies is a sum of local energies  $\epsilon_i$  for each atom, so it is easy to separate the energy into a contribution due to the interior atoms and one due to the buffer atoms. For example, the energy for Model 1 of Fig. 4 can be decomposed as

$$E^{(1)} = \sum_i \epsilon_i = \underbrace{\sum_{i \in I_1} \epsilon_i}_{E_I^{(1)}} + \underbrace{\sum_{i \in B_1} \epsilon_i}_{E_B^{(1)}} \quad (1)$$

where  $I_1$  and  $B_1$  denote the interior and buffer sections of region one, as shown in Fig. 4. The same decomposition can be applied to give  $E^{(2)}$  for Model 2. The total hybrid energy is then obtained by summing the contributions from the two interior regions, neglecting the buffers:

$$E_{\text{hybrid}} = E_I^{(1)} + E_I^{(2)} \quad (2)$$

The artificial surfaces created at the boundary will be much more of a problem when we come to consider embedding a non-local quantum system which is described in the next section.

## 4 Coupling Quantum and Classical Systems

Coupling quantum and classical systems poses significantly greater challenges than combining two classical descriptions of matter. As quantum mechanics is non-local the simple partitioning scheme described above will not work. To overcome this problem we need to provide appropriate boundary conditions for the quantum calculations and find a way to spatially localise their effects.

The quantum mechanical model is assumed to be accurate enough to describe the physics of the region of interest correctly, perhaps using tight binding or an *ab initio* approach. The classical model needs only to correctly capture the basic topology of bonding and give the correct response to small elastic deformations, while remaining inexpensive to compute: empirical interatomic potentials are ideal for this purpose. Furthermore, since we shall use the quantum model anywhere we suspect the classical model will be unreliable, we prefer that the classical model be robust and inexpensive rather than being highly transferable. There has been a great deal of effort in recent years to produce potentials which attempt to model complex processes such as defect formation — generally we have found that such potentials are not useful in a hybrid simulation. We prefer simple potentials such as the Stillinger-Weber model to more complex ones such as EDIP.

The widely used assumption, upon which all quantum/classical hybrid schemes rely, is that the physics is local so that observables can be computed locally, taking into account only atoms which lie within some finite distance of the region of interest. Equivalently, we require that distant trajectories are instantaneously independent. Providing the quantum region is large enough, the trajectories that are important are not affected by the fact that, far away, the system is treated classically. However, it is also necessary, from a practical point of view, that the quantum trajectories can be computed accurately using a small quantum region. Both these conditions are satisfied by the *strong locality* condition:

$$\frac{\partial^n}{\partial \mathbf{r}_j^n} \frac{\partial E_{\text{total}}}{\partial \mathbf{r}_i} \rightarrow 0 \text{ as } |\mathbf{r}_i - \mathbf{r}_j| \rightarrow \infty \quad \forall n \in \mathbb{N}, i \neq j \quad (3)$$

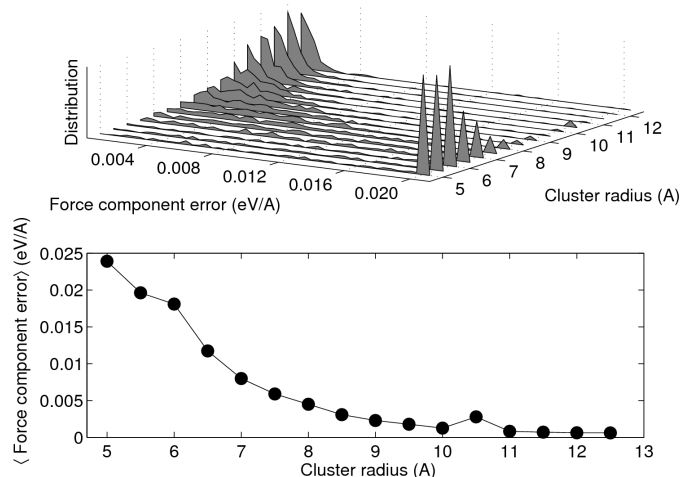


Figure 5. Top: distribution of force component errors at the centre of a finite cluster for a range of cluster sizes. The peaks on the right represent the integrated distribution of errors which are larger than  $0.02 \text{ eV \AA}^{-1}$ . The system is a silicon self-interstitial in a 512-atom cubic cell with periodic boundary conditions, equilibrated at 1400 K. Bottom: the mean of the absolute error in the force components as a function of cluster radius. The peak at  $10.5 \text{ \AA}$  is due to the periodicity of the underlying system. Clusters were terminated with hydrogen atoms. The force model is tight binding, from Ref.<sup>18</sup>. This figure is reproduced from Ref.<sup>19</sup>.

where  $\mathbf{r}_i$  and  $\mathbf{r}_j$  are the positions of atoms  $i$  and  $j$ . This spatial localisation of observables is a stronger requirement than that the density matrix be sparse so that its elements decay rapidly as the separation between two atoms increases. The strong locality assumption can be tested for a particular system by testing the rate of convergence of the force on the central atom of a cluster as the cluster radius is increased. Fig. 5 shows an example of a test of strong locality for silicon using a tight binding force model. Most quantum systems either obey strong locality, or at least the parts of the Hamiltonian that do not, such as long range Coulomb and van der Waals interactions, can be dealt with in a purely classically manner.

Before we consider the details of the coupling strategy, it is appropriate to ask what we want from an ideal hybrid simulation. It is not feasible for the atoms in the quantum region to move as if the whole system were described quantum mechanically, since the classical atoms still move along classical trajectories, and the quantum atoms will respond to the new positions of the classical atoms. Hence, the best we can aim for is for the quantum atoms to behave *instantaneously* as if they are embedded in a fully quantum system.

## 5 The QM/MM Approach

The earliest quantum/classical hybrid simulation was performed by Warshel<sup>1</sup> in 1976 in which they model the reaction of the enzyme lysozyme. Enzyme catalysis is often controlled by large scale motion of macromolecules, with a small active site at which the chemical reaction takes place. Warshel and Levitt noted the need to describe the active site at a quantum mechanical level of detail to give an accurate description of hydrophobic

interactions and hydrogen bonding during catalysis. The electrostatic environment at the active site is determined by the configuration of the entire system of enzyme, substrate and solvent. The long range nature of electrostatic forces in such systems means that atoms far from the active site respond to the presence of a substrate, which in turn causes a change in the local electrostatic environment.

Hybrid methods of this kind, where the dominant interaction is electrostatic, have become known as quantum mechanical/molecular mechanical (abbreviated QM/MM) methods. They have become very popular in the biological and biochemical modelling communities in recent decades. All the fundamental aspects of modern QM/MM techniques were contained in Warshel's pioneering work: the quantum region was chosen very carefully by hand, and the boundary atoms were terminated with a frozen hybrid orbital.

In this section we will give only a brief overview of the QM/MM method which was covered in detail in Professor Thiel's lecture. In the context of the present lecture, DFT embedding should be understood simply as using DFT as the 'QM' method in a QM/MM scheme. It is worth pointing out that compared to quantum chemistry methods, such as Hartree Fock, DFT has a significant disadvantage for embedding schemes. It is known that DFT underestimates bandgaps. One consequence is that the density matrix is less localised in DFT than in quantum chemistry approaches and so DFT embedding is expected to be more sensitive to boundary effects. For reviews of recent developments in the QM/MM field see Ref. 20 and Ref. 21. Within the QM/MM framework, the total energy is the sum of three contributions: the quantum mechanical energy of the quantum region, the classical energy of the rest of the system, and a term representing the interaction between the two. There are two distinct approaches to performing a QM/MM calculation, which differ in their treatment of the interaction between regions: *mechanical embedding* and *electrostatic embedding*. We describe each of these below.

## 5.1 Mechanical Embedding

Mechanical embedding schemes perform quantum calculations for the QM region in the absence of the MM region, treating the interactions between the regions classically. The simplest mechanical embedding scheme is the two-layer ONIOM method,<sup>22</sup> illustrated in Fig. 6. Here the total energy is obtained from three independent calculations:

$$E_{QM/MM} = E_{QM}(QM) + E_{MM}(QM + MM) - E_{MM}(QM) \quad (4)$$

where the subscripts denote the energy model and the function arguments indicate the parts of the system to be included in each calculation. The MM system contains all the atoms and the quantum system contains the atoms of quantum mechanical interest plus *link atoms* used to cap dangling covalent bonds. ONIOM relies on cancellation of errors between the two surface energies.

There are two major drawbacks to the mechanical embedding approach. Firstly it is not always possible to obtain an accurate set of electrostatic MM parameters for atoms in the QM region; this is a particular problem since it is often the unavailability of such parameters which motivates the desire to treat this region quantum mechanically in the first place. Secondly, the scheme ignores perturbations in the electronic structure of the QM region caused by the charge distribution of the MM region. The three layer ONIOM method<sup>23,24</sup> goes some way to solving these problems by introducing an intermediate layer,

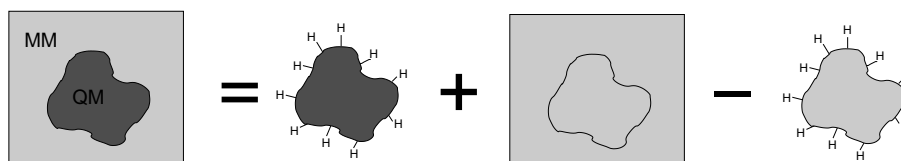


Figure 6. The two-layer ONIOM-style QM/MM scheme. Dark regions are treated with QM and light regions with MM. The termination atoms indicated as H could in fact be a more complex pseudoatom termination.

treated at semi-empirical quantum mechanical accuracy. This allows a consistent treatment of the polarisation of the active site.

## 5.2 Electrostatic Embedding

In an electrostatic embedding scheme the QM calculation is carried out in the presence of the classical charge distribution by adding terms that describe the electrostatic interaction between regions to the QM Hamiltonian. Normally atom centred partial point charges are used, but more advanced techniques employ a multipole expansion of the electric field for increased accuracy. Bonded and van der Waals interactions between the regions are still treated classically.

One problem of the standard electrostatic embedding approach is that classical atoms just outside the quantum region look appear as bare coulomb charges in the quantum calculation. There is a tendency for electron density to unphysically ‘spill-out’ onto these atoms to neutralise these charges. Laio *et al.*<sup>25</sup> have developed an efficient implementation of an electrostatic embedding scheme that addresses this issue by dealing with the short and long range electrostatic interactions differently to avoid spill-out.

## 5.3 Termination of Covalent Bonds

The QM/MM method has been applied fairly extensively to multiscale solid state systems of the types described at the beginning of this chapter. Electrostatic screening is very effective in metals and small band gap insulators, so mechanical embedding schemes are widely used for such systems. Bonded interactions between the QM and MM regions are much more of a problem in the solid state, since for a typical spherical QM region the number of covalent bonds that have to be cut to generate the QM cluster is of the same order as the number of atoms in the region.

To incorporate a quantum mechanical calculation of a subsystem into the total Hamiltonian, these artificially cut bonds must be terminated. There are various methods for doing this, usually based on using hydrogen link atoms or parameterised semiempirical ‘pseudoatoms’ that attempt to mimic the electronic effect of the region outside the subsystem that has been removed. A localised orbital parameterised with calculations on small model systems can be used to provide a quantum mechanical description of the charge distribution around the QM/MM boundary.<sup>26</sup> This approach is less widely used since is not possible to include these hybrid orbitals in a plane wave *ab initio* code.

We have seen in Section 2 that these termination strategies are sufficient to give accurate classical forces, since the classical description of covalent bonding is very near

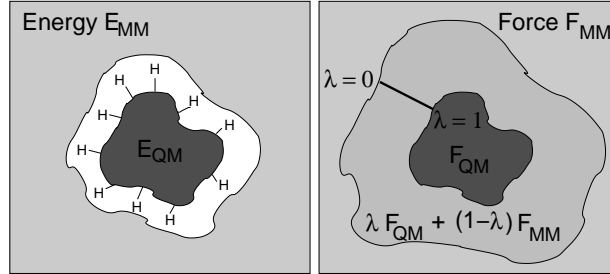


Figure 7. Comparison of QM/MM (left panel) and force mixing (right panel) approaches to the electronic termination problem.

sighted. Quantum mechanics, however, is not a nearest neighbour model, so atoms close to the terminated boundary of the QM subsystem feel an artificial environment, no matter how complex the passivation scheme employed. Moreover, it is impossible to exclude the contribution of the termination atoms to the total quantum mechanical energy of the subsystem. In a typical covalent system the length scale for strong locality of the electronic energy is the order of a nanometre, so any termination method that merely replaces a broken bond with a single atom cannot hope to give accurate forces at the boundary, due to the non-local nature of the quantum mechanical forces.

#### 5.4 Force Mixing

An alternative to the standard QM/MM termination method is to move smoothly from quantum to classical forces over a transition region. This is the *force mixing* technique, where the forces used for the dynamics are interpolated, commonly linearly according to

$$\mathbf{F} = \lambda \mathbf{F}_{\text{QM}} + (1 - \lambda) \mathbf{F}_{\text{classical}} \quad (5)$$

with  $\lambda$  varying from zero on the classical edge of the transition zone to one at the QM edge. Higher order interpolation is also possible. A comparison of traditional QM/MM termination and force mixing is illustrated in Fig. 7.

Compared to the link atom method, force mixing slightly reduces the effect of inaccurate forces on atoms near to the edge of the QM region, since they are reduced in weight and mixed with classical forces. However, since the strong locality length scale is large, the transition zone must be very wide for this to have much of an effect, so large quantum mechanical zones are required.

A major disadvantage of force mixing is that since the forces no longer come from a single Hamiltonian neither energy nor momentum are conserved. The resulting dynamics can be unphysical. The action-reaction principle is not obeyed so, for example, the forces on a dimer spanning the boundary do not sum to zero. This creates a mechanical incompatibility across the boundary, which can lead to instabilities in the dynamics. Nevertheless, force mixing continues to be the most widely used approach for hybrid simulation of solid state systems.

The earliest quantum/classical multiscale fracture simulations were published in 1993 by Spence.<sup>27</sup> They describe their approach as a flexible boundary condition for an *ab initio*

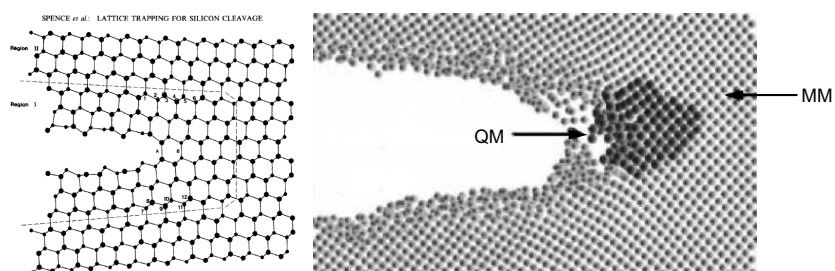


Figure 8. Early hybrid fracture simulation techniques. Left panel: relaxed 324 atom obtained using flexible boundary conditions. Region I (120 atoms) was treated with an *ab initio* method and Region II with an interatomic potential. Reproduced from Ref. 27. Right panel: snapshot from a MAAD simulation of fracture, showing the decomposition of the simulation into finite element (FE), molecular dynamics (MD) and tight binding (TB) regions. Reproduced from Ref. 28.

calculation, but it is effectively a force mixing embedding scheme. Alternate relaxations of the two regions illustrated in Fig. 8a were performed, with an overlap buffer to ensure self consistency. Some years later, Broughton<sup>28</sup> proposed the MAAD (macroatomistic *ab initio* dynamics) method which couples finite elements, molecular dynamics and semiempirical tight binding in a QM/MM approach to model crack propagation; a snapshot of the dynamics is shown in Fig. 8b. Pseudoatom terminator ‘silogens’ designed to behave like monovalent silicon atoms were used to terminate the tight binding region and a force mixing embedding approach was used.

Ogata’s group has applied the ONIOM method to the simulation of cracks,<sup>29</sup> surface oxidation<sup>30</sup>, and more recently they have investigated the effect of water on the initiation of corrosion induced cracks.<sup>31</sup> The group uses an improved version of ONIOM called the buffered-cluster method.<sup>32</sup> The QM region is cut out as normal, but then buffer atoms are added to terminate broken covalent bonds. The buffer is then relaxed using the classical force model, resulting in a relaxed buffered cluster which gives better surface error cancellation since it is closer to the equilibrium bulk structure.

## 5.5 Multiple Layer Termination

In 2001, Bernstein and Hess<sup>33</sup> proposed a modified treatment of the quantum zone boundary that addresses the electronic termination problem. They used a Green’s function technique to create a *transition zone* with a thickness of several atomic layers which is included in the quantum mechanical calculation. Forces from this zone are not included in the dynamics. This method was later employed in a hybrid classical and tight binding simulation,<sup>34</sup> referred to as the DCET (dynamic coupling of empirical potential and tight binding) method. The combination of transition zone and force mixing gives accurate quantum mechanical forces and allowed the QM region to be moved during a simulation for the first time. However, the force mixing technique requires a large QM region, making the method difficult to scale up to a full *ab initio* calculation.

There is an alternative, more straightforward, termination strategy: we can obtain accurate *forces* for all atoms in the quantum region by using a wider buffer region. If we include a thick enough shell of nominally classical atoms in the quantum calculation, then

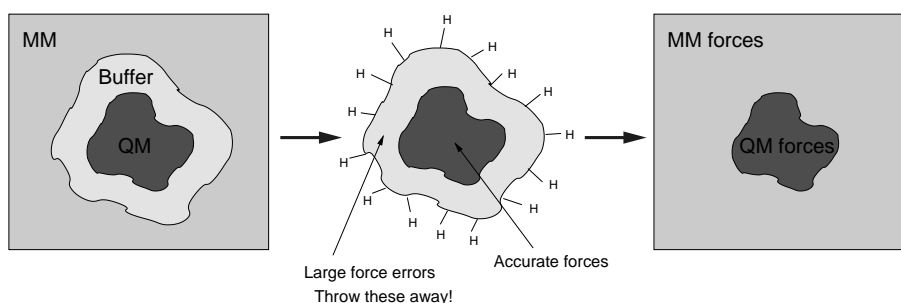


Figure 9. The finite buffer termination strategy. Forces on the atoms in the buffer region are discarded to give accurate hybrid forces on all atoms (right hand side).

the forces on the QM atoms themselves will be accurate. Since these forces are local quantities, we can easily discard the contaminated termination region and keep only the forces on the original QM atoms. This finite buffer scheme, illustrated in Fig. 9, is a major ingredient of the ‘Learn on The Fly’ hybrid method which will be the primary topic of the lecture.

These multiple layer termination approaches can solve the electronic termination problem, but there will still be a mechanical incompatibility across the boundary. If we used forces from the finite buffer scheme to do molecular dynamics, the resulting trajectories could be unstable, exactly as in the force mixing approach discussed above.

## 6 Summary

This lecture has introduced hybrid modelling techniques and reviewed a number of approaches which allow simultaneous simulation of coupled quantum and classical systems. We have seen that the fundamental difficulty of constructing such a hybrid modelling scheme lies in finding an effective treatment of the boundary. This is a particular problem in solid state systems, where many covalent bonds have to be cut to form the QM cluster and this has restricted the application of the QM/MM method. The problem can be divided into the electronic termination problem, which can be solved by discarding the inaccurate forces in a buffer zone at the edge of the QM region, and the mechanical matching problem. A solution to this mechanical mismatch is the basis of the ‘Learn on The Fly’ method.

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