Final Technical Report

**Multiscale Design of Advanced Materials based on
Hybrid Ab Initio and Quasicontinuum Methods**

**DOE Contract Number: FG0205ER25706
08/15/2005–08/14/2009**

**Principal Investigator: Mitchell Luskin, University of
Minnesota
co-Principal Investigators: Richard James, Ellad Tadmor**

**206 Church St SE
School of Mathematics
University of Minnesota
Minneapolis, MN 55455
Telephone: 612-625-6565
Email: luskin@math.umn.edu**

**Office of Advanced Scientific Computing Research (ASCR)
Office of Science Technical Contact: Sandy Landberg,
Sandy.Landsberg@science.doe.gov**

Contents

1	Analysis and Mathematical Foundation of the QC Method and other Multiscale Methods	1
2	Iterative Solution of the QCF Equilibrium Equations	3
3	Error Estimators and Adaptivity	3
4	Finite-Temperature and Quasicontinuum Dynamics	4
5	Thermostats	4
6	Cauchy-Born Kinematics for Phase Transforming Materials	5
7	QC for Objective Structures	6
8	Coupling QC with Quantum Mechanics	7

This report summarizes work done by researchers at the University of Minnesota under the DOE Project *Multiscale Design of Advanced Materials based on Hybrid Ab Initio and Quasicontinuum Methods*. We developed a new mathematical framework for the static quasicontinuum method from which optimal order error estimates were derived. These, in turn, guided the further development of the method. The method itself was integrated with an *ab initio* calculation of potential energy. The method was applied to the mechanical behavior of complex crystals undergoing deformations with length scales previously unattainable. Detailed descriptions of accomplishments are given below.

1 Analysis and Mathematical Foundation of the QC Method and other Multiscale Methods

We have developed mathematical analysis to guide the development and assessment of multiscale quasicontinuum (QC) methods. Algorithmic simplicity and efficiency are certainly important for implementation and application, but concerns about accuracy have led to the search for a consistent scheme. Since the forces on all of the atoms in a lattice that has been deformed by a uniform strain are zero, a quasicontinuum approximation can be said to be consistent if there are no forces on the representative atoms

for a lattice that has been deformed by a uniform strain. Nonzero residual forces are referred to as “ghost forces.”

Quasicontinuum energies have been derived that are consistent for planar atomistic to continuum interfaces by utilizing special calculations in an interfacial region, but there is still no known consistent quasicontinuum energy for general nonplanar atomistic to continuum interfaces, other than the computationally intensive constrained quasicontinuum energy. We investigated two solutions to this dilemma. The first solution resulted from our discovery that ghost forces are confined to the interface and are oscillatory in space [11,13]. Thus, the effect of the ghost forces on the deformation computed by a quasicontinuum energy nearly cancel and have a small effect on the error. We obtained optimal order error estimates for a model problem similar to the quasicontinuum energy of Tadmor, Ortiz, and Phillips that the deformation does converge at the rate $O(h)$ in the l^∞ and $w^{1,1}$ norms for a properly scaled limit even though the atomistic-to-continuum coupling is not consistent in the interfacial region [13].

The second solution for static problems is given by the *force-based quasicontinuum method* (QCF). QCF is an attractive choice for quasicontinuum approximation because it is a consistent scheme [11] that is algorithmically simple: the force on each representative atom is given by either an atomistic calculation or a continuum finite element calculation. The algorithmic simplicity of the force-based quasicontinuum method has allowed it to be implemented with adaptive mesh refinement and atomistic to continuum model selection algorithms [2, 3]. The trade-off for the consistency and algorithmic simplicity of QCF is that it does not give a conservative force field, although it is close to a conservative force [11].

To compare QC with other multiscale methods, we implemented and studied the accuracy of fourteen leading multiscale methods (including QC) and benchmarked their efficiency for a realistic boundary-value problem [26]. The main conclusions from this study were:

1. force-based methods are more accurate than energy-based methods (although a simple ghost force correction can in most cases eliminate this advantage);
2. energy-based methods are faster than force-based methods;
3. strong compatibility is faster than weak compatibility;
4. handshake regions tend to slow down methods without improving accuracy.

Project Publications: [11, 13, 14, 22, 26]

2 Iterative Solution of the QCF Equilibrium Equations

We proved in [11] that the QCF equilibrium equations have a unique solution under physically appropriate conditions. For Lennard-Jones next-nearest-neighbor interactions, we showed that unique solutions exist for external forces that extend the system nearly to its tensile limit. We then gave an analysis of the convergence of the iterative method used in Tadmor’s QC code to solve the equilibrium equations for the force-based quasicontinuum approximation. We showed that the iteration is a contraction and gave an analysis for its convergence rate that theoretically demonstrated its rapid convergence.

For quasi-static loading, we gave an analysis to determine an efficient strategy for the parameter step size and number of iterations at each parameter to achieve a solution to a required tolerance [12]. We reported computational experiments that exhibit fracture before the actual load limit if the parameter step size is too large.

Project Publications: [10, 11]

3 Error Estimators and Adaptivity

We developed and analyzed a goal-oriented a posteriori error estimator for the atomistic-continuum modeling error in the QC method [2, 3]. Based on this error estimator, we developed an algorithm which adaptively determines which regions need to be modeled atomistically to be able to compute a quantity of interest to within a given tolerance. We applied the algorithm to the computation of the structure of a crystallographic defect described by a Frenkel-Kontorova model and obtained numerical results that show that our method gives an effective estimate of the error and a nearly optimal atomistic-continuum modeling strategy

In regions of the crystal with a highly nonuniform deformation such as around defects, every atom must be a representative atom to obtain sufficient accuracy, but the mesh can be coarsened away from such regions to remove atomistic degrees of freedom while retaining sufficient accuracy. In [4], we presented an error estimator and a related adaptive mesh refinement algorithm for the quasicontinuum approximation of a generalized Frenkel-Kontorova model that enables a quantity of interest to be efficiently computed to a predetermined accuracy.

Project Publications: [2–4]

4 Finite-Temperature and Quasicontinuum Dynamics

Two significant improvements to the finite-temperature version of the QC method (hot-QC) were achieved: (1) implementation of more accurate thermostating (described below in the next section), and (2) a correction for a mesh-dependency effect we refer to as “mesh entropy”. In a hot-QC simulation atoms (nonlocal representative atoms) and nodes (local representative atoms) are combined into a single dynamical system and tied to a thermostat to maintain a given equilibrium temperature. The free energy of the atoms removed from the continuum region is estimated using a local harmonic approximation, while the atoms in the atomistic region directly sample phase through their dynamical trajectories. The combined result provides a good approximation to the free energy of the entire system, however an error is introduced by the dynamical motion of the nodes in the continuum region. This results in an additional non-physical entropy related to the mesh structure. This is the mesh entropy. We derived an analytical approximation for this quantity which we subtract from the total free energy. We proved that with this correction, hot-QC reproduces exact phase averages to second-order accuracy in temperature [25].

Project Publications: [25]

5 Thermostats

The Nosé-Hoover thermostat is a deterministic dynamical system designed for computing phase space integrals for the canonical Gibbs distribution. Newton’s equations are modified by coupling an additional reservoir variable to the physical variables. The correct sampling of the phase space according to the Gibbs measure is dependent on the Nosé-Hoover dynamics being ergodic. In [19], we gave the first rigorous proof that the Nosé-Hoover thermostat does not give an ergodic dynamics for the harmonic oscillator when the “mass” of the reservoir is large. Our proof of non-ergodicity used KAM theory to demonstrate the existence of invariant tori for the Nosé-Hoover dynamical system that separate phase space into invariant regions. We presented numerical experiments motivated by our analysis that seemed to show that the dynamics is not ergodic even for a moderate thermostat mass.

These lessons learned from the Nosé-Hoover study prompted us to revisit the thermostating used in hot-QC. In the original formulation of hot-QC, a Nosé-Poincaré thermostat was used to couple the hybrid atomistic-continuum model to a heat bath held at a constant temperature. The Nosé-Poincaré thermostat is similar to Nosé-Hoover, but it results in a sys-

tem with Hamiltonian dynamics, which has the advantage that symplectic, time-reversible, integrators can be constructed for it. It is also believed to have enhanced ergodicity properties. We studied the performance of Nosé-Poincaré thermostating for a simple problem of a square atomistic region embedded in a surrounding continuum. We found that the atomistic region remained at a higher temperature than the surroundings even after very long times. This may be an indication of non-ergodic behavior of the system. In contrast, a Langevin thermostat quickly brought both the atomistic and continuum regions to the desired temperature [25].

Project Publications: [19, 20, 25]

6 Cauchy-Born Kinematics for Phase Transforming Materials

One of the stated objectives in our proposal was to extend the QC method to multilattices (i.e., crystals in which the unit cell has more than one atom). Many important technological materials as well as materials that undergo phase transformations have this structure. The main difference is that the Cauchy Born (CB) kinematics, which are used in QC to obtain the constitutive response in continuum regions, must be modified. For a simple crystal, CB kinematics state that the atoms are mapped according to the continuum field. For a multilattice the shifting of the basis atoms must also be accounted for. This is straightforward to do, however a question arises as to which description of the crystal structure should be used with CB kinematics.

Traditionally, CB kinematics has been interpreted as being applied to the simplest periodic structure that reproduces the crystal. This was the approach adopted in the original multilattice QC implementation of Tadmor and co-workers that was later applied to a number of problems of interest. However, as pointed out by Pitteri and Zanzotto, the traditional definition of the CB rule can “fail” since some deformations require an increase in the periodic size of the unit cell. The problem is that the minimum required cell size cannot be known a priori. Detection of such period extensions can be critical in many cases where martensitic phase transformations occur in the material.

To address this issue within QC we developed a new method in which a phonon stability analysis is performed locally within each finite element in the continuum region at the end of each load step. This analysis detects the onset of period extension and identifies a new minimal lattice description; a methodology referred to as *Cascading Cauchy-Born (CCB) kinematics*. The method was validated on 1-dimensional test problems [9, 10] and then extended to higher dimensions and used with an effective interaction po-

tential material model for a prototypical shape memory alloy to simulate a complete shape memory cycle [24]. The results capture both temperature- and stress-induced martensitic transformations.

In addition to the methodological innovation described above, the QC implementation was also extended to accommodate multilattice crystals. In particular, efficient methods for constructing deformed multilattice crystals in the continuum region based on lattice reduction techniques were developed [1].

Project Publications: [1, 9, 10, 24]

7 QC for Objective Structures

The main simplification that is exploited by QC methods is that, away from defects, the main deformation of the material is a small perturbation of a perfectly periodic configuration. We noticed that the same simplification is possible for a much broader class of structures besides crystals. These include various nanostructures that comprise some of the most interesting molecular structures under study today, that have the possibility for entirely new materials with exceptional strength and unusual combinations of electromagnetic/optical properties, including unusual forms of ferroelectricity and ferromagnetism, and unusual transport properties. These structures for which an extension of QC methods is possible are termed *objective structures*.

Objective structures are structures composed of identical molecules, each containing atoms numbered $1, \dots, M$. This structure is an objective structure if the atomic environment of atom $k \in \{1, \dots, M\}$ of one molecule can be mapped precisely onto the atomic environment of atom k of a different molecule by an orthogonal transformation and translation. Objective structures include C_{60} , single-walled carbon nanotubes of any chirality, many of the basic proteins of biology like actin and collagen, the parts of many viruses, and many nanostructures now being synthesized by methods of self-assembly. These are important materials for QC methods: for example, the exceptional strength of carbon nanotubes – 100 times the tensile strength of steel at 1/6 the density – can only be understood by understanding the formation and propagation of defects in them.

We have begun this work by developing the underlying technology for Objective-QC. First, we gave an explicit formula for the positions of every atom of every objective structure [18]. Besides the structures mentioned above, there are many interesting structures given by these formulas that are nonstandard, and provide a basis for the systematic search for new nanostructures. These formulas with their explicit parameter dependence have been proven to be extremely useful. We developed an computational ap-

proach for Objective-QC in [16].

We have shown that first principles calculations of electronic structure based on density functional theory can be simplified for objective structures in much the same way as for crystals [5,17,27]: periodic boundary conditions are replaced by what we call *objective boundary conditions*. This opens the way for an *ab initio* QC method for objective structures. In the case of the finite groups, a very sophisticated code has been developed. Interestingly, it shows exceptional scaling behavior even for clusters with no symmetry at all. This is partly due to the choice of bases that, unlike with plane wave approaches, do not waste a lot of basis elements calculating the value 0.

In the dynamic case we have found an exact time-dependent invariant manifold of the equations of molecular dynamics that can be exploited for objective structures [7,15]; this in itself leads to a multiscale method, but also paves the way for a hot-QC method for objective structures. This method has revealed for the first time accurate pictures of twisted and bent nanotubes and their primary instabilities. These results show that methods based on Tersoff or Tersoff-Brenner semi-empirical potentials, or continuum plate and shell theories do not generally predict accurately the shape changes in bending or torsion, or even the correct instabilities [27,28]. We have also given predictions of the behavior of bandgap with deformation, an understanding that is completely inaccessible to either the semi-empirical or continuum methods. These results have important implications for proposed sensing applications of carbon nanotubes.

These results have been generalized to cases of short and long range electrostatic interactions [6]. This is important for many functional materials.

Project Publications: [6–8,15–17,21,27–29]

8 Coupling QC with Quantum Mechanics

Another emphasis of our proposal was to develop methods for incorporating more accurate quantum mechanical (QM) descriptions of bonding within QC. A new approach to doing this was developed and is currently being tested. As opposed to our earlier “QCDFT” methodology, which is based on approximating the interaction energy between the QM region and the classical QC region where interatomic potentials (IP) are used, in the new approach we incorporate a novel method recently suggested by Benstein and Csanyi that enables the definition of *localized site energies* for a QM tight-binding method. This new approach, referred to as “QUIP”, provides accurate forces with minimal effects from the interface between the QM and IP regions, and relies on fewer assumptions about the nature of bonding and the chemical species involved than QM/MM methods used in quantum chemistry. We are currently comparing results using the new QC/QUIP

Figure 1: A QC/QUIP simulation of a crack tip in Si. The yellow/green region is the quantum mechanical (tight binding region), the red/white region is the classical QC atomistic (nonlocal) region, the blue/light blue region is the beginning of the QC continuum (local) region that extends a long way away from the crack.

method with the previous QCDFE approach for several systems, including a crack tip and a dislocation in Al and Si [23]. An example of a QC/QUIP simulation of a crack in Si is shown in Fig. 1.

Project Publications: [23]

References

- [1] M. Arndt, V. Sorkin, and E. B. Tadmor. Efficient algorithms for discrete lattice calculations. *J. Comp. Phys.*, 228:4858–4880, 2009.
- [2] Marcel Arndt and Mitchell Luskin. Goal-oriented atomistic-continuum adaptivity for the quasicontinuum approximation. *International Journal for Multiscale Computational Engineering*, 5:407–415, 2007.
- [3] Marcel Arndt and Mitchell Luskin. Error estimation and atomistic-continuum adaptivity for the quasicontinuum approximation of a Frenkel-Kontorova model. *SIAM J. Multiscale Modeling & Simulation*, 7:147–170, 2008.
- [4] Marcel Arndt and Mitchell Luskin. Goal-oriented adaptive mesh refinement for the quasicontinuum approximation of a Frenkel-Kontorova model. *Computer Methods in Applied Mechanics and Engineering*, 197:4298–4306, 2008.
- [5] Amartya S. Banerjee, Ryan S. Elliott, and Richard D. James. A spectral scheme for Kohn-Sham density functional theory of clusters. preprint. submitted to J. Computational Physics.
- [6] K. Dayal and R. D. James. Continuum limits of objective structures with short-range and coulombic interactions. preprint.
- [7] Kaushik Dayal and Richard D. James. Nonequilibrium molecular dynamics for bulk materials and nanostructures. *Journal of the Mechanics and Physics of Solids*, 58(2):145 – 163, 2010.
- [8] Kaushik Dayal and Richard D. James. Design of viscometers corresponding to a universal molecular simulation method. *J. Fluid Mech.*, 461:691, 2012.
- [9] M. Dobson, R. S. Elliott, and E. B. Tadmor. A quasicontinuum for complex crystals. In *Proceedings of the Third International Conference on Multiscale Materials Modeling, MMM-III, Freiburg*, September 18–22, 2006.

- [10] M. Dobson, M. Luskin, R. S. Elliott, and E. B. Tadmor. A multilattice quasicontinuum for phase transforming materials: Cascading Cauchy Born kinematics. *Journal of Computer-Aided Materials Design*, 14:219–237, 2007.
- [11] Matthew Dobson and Mitchell Luskin. Analysis of a force-based quasicontinuum approximation. *Mathematical Modelling and Numerical Analysis*, 42:113–139, 2008.
- [12] Matthew Dobson and Mitchell Luskin. Iterative solution of the quasicontinuum equilibrium equations with continuation. *Journal of Scientific Computing*, 37:19–41, 2008.
- [13] Matthew Dobson and Mitchell Luskin. An analysis of the effect of ghost force oscillation on quasicontinuum error. *Mathematical Modelling and Numerical Analysis*, 43:591–604, 2009.
- [14] Matthew Dobson and Mitchell Luskin. An optimal order error analysis of the one-dimensional quasicontinuum approximation. *SIAM. J. Numer. Anal.*, 47:2455–2475, 2009.
- [15] Traian Dumitrica and Richard D. James. Objective molecular dynamics. *J. Mech. Phys. Solids*, 55:2206–2236, 2007.
- [16] Ye. Hakobyan, E. B. Tadmor, and R. D. James. Objective quasicontinuum approach for rod problems. *Phys. Rev. B*, 86:245435, 2012.
- [17] R. D. James. Objective structures. *J. Mech. Phys. Solids*, 54:2354–2390, 2006.
- [18] R. Elliott K. Dayal and R. D. James. Objective formulas. *preprint*.
- [19] Frédéric Legoll, Mitchell Luskin, and Richard Moeckel. Non-ergodicity of the Nosé-Hoover thermostatted harmonic oscillator. *Archive for Rational Mechanics and Analysis*, 184:449–463, 2007.
- [20] Frédéric Legoll, Mitchell Luskin, and Richard Moeckel. Non-ergodicity of Nosé-Hoover dynamics. *Nonlinearity*, 22:1673–1694, 2009.
- [21] Liping Liu, R. D. James, and P. H. Leo. Periodic inclusion-matrix microstructures with constant field inclusions. *Metall. Trans.*, 38A:781–787, 2007.
- [22] Mitchell Luskin and Christoph Ortner. An analysis of node-based cluster summation rules in the quasicontinuum method. *SIAM. J. Numer. Anal.*, 47:3070–3086, 2009.

- [23] V. Sorkin, N. Bernstein, G. Csanyi, and E. B. Tadmor. Coupled quantum mechanics and quasicontinuum simulations of mechanical properties of defects. in preparation.
- [24] V. Sorkin, R. S. Elliott, and E. B. Tadmor. A local quasicontinuum method for 3D multilattice crystalline materials: Application to shape-memory alloys. *Model. Sim. Mat. Sci. Eng.*, 2014. in press.
- [25] E. B. Tadmor, F. Legoll, W. K. Kim, L. M. Dupuy, and R. E. Miller. Finite-temperature quasicontinuum. *Appl. Mech. Rev.*, 65:010803, 2013.
- [26] E. B. Tadmor and R. E. Miller. A unified framework and performance benchmark of fourteen multiscale atomistic/continuum coupling methods. *Modelling Simul. Mater. Sci. Eng.*, 17:053001, 2009.
- [27] D.-B. Zhang, R. D. James, and T. Dumitrica. Electromechanical characterization of carbon nanotubes in torsion via symmetry adapted tight-binding objective molecular dynamics. *Physical Review B*, 80(11):115418, 2009.
- [28] D.-B. Zhang, R. D. James, and T. Dumitrică. Plasticity onset and kink dynamics in carbon nanotubes under torsion. *Physical Review B*, 80(11):115418, 2009.
- [29] Zhiyong Zhang, R. D. James, and Stefan Müller. Energy barriers and hysteresis in martensitic phase transformations. *Acta Materialia (Invited Overview)*, 57:2332–4352, 2009.