MULTISCALE ATOMISTICS FOR DEFECTS IN ELECTRONIC MATERIALS

Kaushik Dayal*[a)] & Jason Marshall*
*Carnegie Mellon University, USA

Summary Defects in electronic materials play a critical role. However, atomistic calculations of defect structure in realistic settings pose two challenges: (i) charge interactions are long-range, and (ii) electric fields exist outside the specimen in all of space. We present a multiscale method to calculate defect atomic structure and response with electrostatic interactions. The key ideas are (i) application of continuum limits of charged lattices, and (ii) Dirichlet-to-Neumann map to transform from all-space to a finite domain.

OVERVIEW AND PROBLEM FORMULATION

Defects in electronic solids are often critical to their functionality; important examples include dopants in semiconductors and domain walls in ferroelectrics. Additionally, mechanical defects such as cracks and dislocations are important limiters of reliability in these materials. Hence, it is important to understand the atomistic structure and properties of defects in realistic, non-periodic settings, e.g. at free surfaces, near electrodes, under non-uniform electric field, etc. This however presents two key challenges in electronic materials: first, there are long-range Coulombic interactions between *every* pair of charges in the system, and second, there are stray electric fields outside the specimen in all of space.

We aim is to minimize the energy E of a system of atoms/ions that interact through standard short-range interatomic forces as well as long-range Coulombic interactions. This can be written:

$$\min_{\{\boldsymbol{x}_i\}} E, \quad E = \underbrace{\sum_{i,j} \psi(\{|\boldsymbol{x}_i - \boldsymbol{x}_j|\})}_{\text{short-range}} + \underbrace{\sum_{i,j} \frac{Q_i Q_j}{|\boldsymbol{x}_i - \boldsymbol{x}_j|}}_{\text{electrostatic}} \tag{1}$$

Here, $\boldsymbol{x}_i$ and Q_i are the position and charge respectively of atom/ion i, and $\psi(\cdot)$ is the short-range interatomic potential. We rewrite E in terms of the electrostatic potential field ϕ:

$$E = \sum_{i,j} \psi(\{|\boldsymbol{x}_i - \boldsymbol{x}_j|\}) + \int_{\mathbb{R}^3} |\nabla\phi|^2 \, dV \tag{2}$$

The field ϕ is obtained from a solution of the electrostatic equation $\nabla^2\phi = \rho(\{\boldsymbol{x}_i, Q_i\})$ on $\mathbb{R}^3$, subject to $\phi = V$ on the electrodes, and $\nabla\phi(\boldsymbol{r}) \to 0$ as $|\boldsymbol{r}| \to \infty$.

The goal is to minimize the energy of a specimen consisting of a relatively large number of atoms/ions. However, complete atomic resolution is required only in the vicinity of the defect, and adaptive and consistent coarse-graining can be used in regions away from the defect where the deformation is close to uniform. This coarse-graining enables the treatment of large samples with complex boundary conditions in the far-field.

TECHNICAL APPROACH

The additive decomposition of short-range and long-range forces enables us to exploit tailored strategies for each contribution individually. The atomic interactions involving $\psi(\cdot)$ are nonlinear but short-range. These are treated using the standard quasicontinuum method [1]. The Coulombic interactions between ions have complementary features: the interactions are long-range but linear. We exploit rigorous analytical formulas arising from continuum limits of charged lattices [2] to develop a coarse-grained numerical scheme [3] for charge interactions. Finally, we use Dirichlet-to-Neumann maps to consistently transform the exterior electrostatics problem due to external electric fields to a finite domain [4].

Short-Range Atomic Interactions

The Quasicontinuum method is a multiscale approach to predict defect structure *when only short-range forces are present*. We apply it to the short-range calculation. There are 2 key steps. First, reduction of number of degrees of freedom using the ansatz $\boldsymbol{x}_i = \sum_a \boldsymbol{x}_a N_a(\boldsymbol{x}_i)$, where $N_a(\cdot)$ is an interpolating function and $\boldsymbol{x}_a$ is the displacement of the *nodal* atom a. The second step is to efficiently perform lattice sums far away from the defect using the Cauchy-Born rule.

[a)]Corresponding author. E-mail: kaushik@cmu.edu

Long-Range Coulombic Interactions

The key multiscale step, motivated by rigorous results, is to replace the rapidly varying atomic-level charge distribution by the much smoother polarization density $\boldsymbol{p}$

$$\nabla^2\phi = \nabla\cdot\boldsymbol{p}, \quad \boldsymbol{p}(\boldsymbol{x}) := \int_{\square} \boldsymbol{x}\rho(\boldsymbol{x},\boldsymbol{x}/\epsilon)\,dV$$

where $\rho(\boldsymbol{x},\boldsymbol{x}/\epsilon)$ is a 2-scale function, varying both at the atomic lengthscale ϵ as well as at the macroscopic lengthscale $\boldsymbol{x}$. However, $\boldsymbol{p}$ is an integral over the atomic unit cell $\square$ and varies only at the macroscopic lengthscale. The Poisson equation thus defined can be solved with a discretization that is atomically-fine only near the defect.

Transforming the Exterior Electrostatics Problem

The key idea is apply the Dirichlet-to Neumann map (DtN) to transform the exterior electrostatics problem to a finite domain with "effective" boundary conditions. Standard approaches to this are possible, but most available algorithms are direct rather than iterative. Due to the nonlinearity inherent to the problem from short-range atomic interactions, we require a large number of iterations and direct DtN solves at each iteration would be prohibitively expensive. Hence, we formulate an iterative DtN [4] to enable coupling of the iterations due to the nonlinearity to the iterations of the DtN. Consequently, every iteration is much less expensive and the large number of iterations required by the nonlinear short-range interactions is feasible.

PRELIMINARY RESULTS

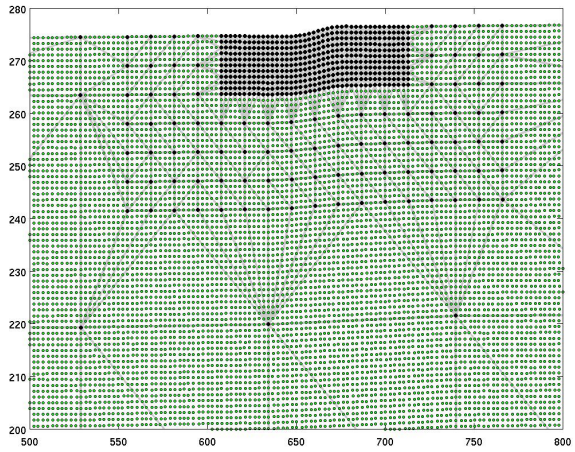

Figure 1. Deformation of the crystal. The mesh is superposed and dark atoms are nodal atoms. The coarse-graining away from the localized deformation is easily visible.

We apply the method to model the response of a ferroelectric single-crystal specimen with an extremely localized electrical field applied at a free surface through an electrically charged tip. Figure 1 shows the atomic configuration near the free surface of the ferroelectric. The specimen extends to a large distance horizontally and downwards, and the top surface is a free surface. When no field is applied, the ferroelectric has a spontaneous polarization oriented to the left and the free surface is flat. As the electric field is applied, it causes both an electrical response as well as a mechanical distortion due to the electromechanical coupling.

Figure 2 shows the induced electrical response, i.e. the component of polarization in the vertical direction which is initially entirely absent (right), and the mechanical response (left). The mechanical response shows an interesting double-lobe structure and almost no stress directly beneath the charged tip. This is not observed in calculations of a similar setting using continuum phase-field models.

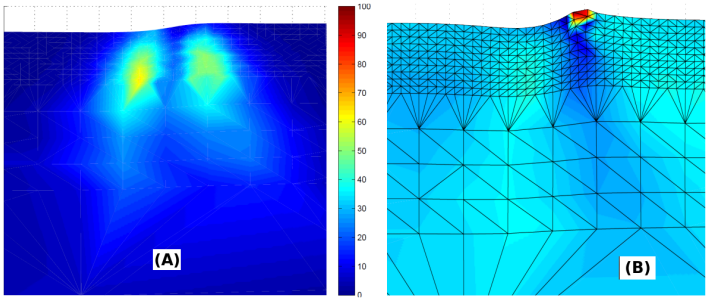

Figure 2. Left: Mechanical stress measure showing 2 lobes; right: Polarization magnitude in the vertical direction.

References

[1] E. Tadmor, R. Miller. *The quasicontinuum method: Overview, applications and current directions*. J. Comp.-Aided Mat. Des., 9:203–239, 2002.

[2] R. D. James and S. Muller. *Internal variables and fine-scale oscillations in micromagnetics*. Cont. Mech. Thermodyn., 6:291–336, 1994.

[3] J. Marshall and K. Dayal. *Atomistic-to-continuum multiscale method for defects in crystals with long-range electrical interactions*. Preprint (2011).

[4] L. Yang and K. Dayal. *A Completely Iterative Method for the Infinite Domain Electrostatic Problem with Nonlinear Dielectric Media*. J. Comput. Phys., 230:7821, 2011.