The use of atomic level stress to characterize the structure of irradiated iron

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Abstract. The behaviour of irradiated material near a primary knock on atom immediately after impact is of great importance for designing reactor materials. Currently, molecular dynamics simulations with classical force fields provide the foundation for understanding the resulting cascade. However, modern density functional calculations can now treat large enough numbers of atoms that they can provide additional details of the magnetic and electronic nature of irradiated samples. In this paper we calculate from first principles the atomic level stresses for an instantaneous configuration following the initiation of a low energy cascade in iron.

1. Introduction

Radiation damage occurs when a highly energetic particle incident on a solid transfers its energy to the atoms in the solid displacing atoms from their original crystal lattice positions through absorption of energy in excess of the displacement threshold energy. This displacement of atoms creates vacancy (V) and interstitial (I) defects in pairs, Frenkel pairs. The initially displaced atom is called the primary knock-on atom (PKA); it interacts with other atoms in the crystal displacing them from their lattice sites and thereby generating a displacement cascade. Thus, irradiating a solid with ions or neutrons creates a cascade of Frankel pairs. This process continues until the crystal absorbs all the energy of the incident particle. In the case of iron, the cascade continues to generate defects until no single atom has energy in excess of the displacement threshold energy (40 eV in Fe) to cause further displacements. The remaining kinetic energy is eventually taken away by lattice phonons.

A complex sequence of events is initiated by the irradiation, which produces mainly undesirable changes in the material’s properties. The radiation damage caused by fast neutrons to solids is due to the direct transfer of kinetic energy in the range of several tens of keV to the lattice atoms. This transfer happens on a length scale of nanometers and in the time scale of sub-picoseconds (ps) to a few ps. Figure 1 shows the evolution of Frenkel pairs in displacement cascades in alpha iron at 100K for different PKA energies [1].
Figure 1. The calculated (Modified Finnis and Sinclair [2] molecular dynamics (MD)) number of Frenkel pairs is shown as a function of time after cascade initiation for a series of PKA energies.

A detailed and basic understanding of the initial damage event itself is very important to understand all the later events and the changes caused by radiation damage in microstructure and mechanical properties.

2. Local energy and pressure

A general first principles approach to the problem of defining the local stress [3] is to start by defining a first principles local energy associated with each atom in the system. The local stress can then be determined from the response of the local energy to the application of small affine strains to the system. The local stresses and elastic moduli can be determined by the first and second derivatives of the local energy with respect to strain. In this paper we make a single, simple choice for the definition of local energy and observe the correlation of several local quantities with the local pressure. The local stress has been used for systems that interact through classical potentials to explain glass stability [4] and as the basis for an equipartition theorem [5] for local elastic energy in MD simulations. For classical pair potential systems the local stress has been derived on the basis of pairwise forces without resorting to the definition of a local energy [6]. This result has been extended to the Embedded Atom Method [7], which has force fields that include many-body interactions. For both these types of force fields, expressions can be obtained by first defining a local energy and then evaluating the variation of the local energy with respect to strain, for example an atom can be assigned a local energy given by half the energy of bonding with each atom within the range of the potential.

In the ideal gas limit there are no forces and the only stress is the pressure that results from collision with the walls of the container. In another extreme case, a zero temperature solid, nuclei are stationary and forces are present but sum to zero on each atom. Even though the forces on each atom sum to zero they can contribute to large local stresses, for example: in intermetallic compounds, defects in single component materials, or even in single component perfect crystals if the volume differs from the equilibrium value. Here we will ignore the pressure due to the motion of the nuclei and will evaluate the contribution from the electron bonding. This bonding includes electron but not nuclear kinetic energy.

The energy of the electron-nuclear system is the foundation of Density Functional Theory (DFT) based calculations [8]. The energy is often separated into the kinetic energy, $T_s$, of an auxiliary system
with the same electron density as that of the interacting ground state, the classical electrostatic energy of all charges in the system, $U_{\text{c}}$, and correction energy, $E_{\text{xc}}$, that accounts for the correlation (including that which results from exchange) between electrons. The correlation affects both kinetic and electrostatic energy. The challenge is to further decompose the energy into local contributions that have the greatest descriptive power.

In the Local Density Approximation (LDA) [9], $E_{\text{xc}}$ is defined locally; this makes the association with an atomic site apparently straightforward. Although we will take local $E_{\text{xc}}$ to be given by the integral over the local atomic volume of the product of the electron density and its energy density, we acknowledge that other assignments are possible especially when approximations beyond LDA are considered.

The kinetic energy can be evaluated as the negative of the expectation value of the Laplacian. A natural choice for the local contribution is that obtained by limiting the expectation value integral to the volume of the atomic site. An alternative choice is based on the symmetric form of the kinetic energy, which is the integral of the modulus squared of the gradient of the wavefunction. The two definitions differ by a surface integral that vanishes over the boundary of the supercell or at a boundary at infinity if the system is finite. We argue in favor of the asymmetric form because: 1) it has the form of an expectation value, 2) it conforms to our physical notions, that the kinetic energy contribution is highest at the potential minimum (as opposed to zero for the symmetric form) for a harmonic oscillator in its ground state, and 3) it is more closely associated with the sum of eigenvalues, a quantity that has proved very useful in qualitative descriptions of bonding.

Because the classical electrostatic force is pairwise, the underlying nature of the classical electrostatic energy is that of a pair interaction. It can be recast as a local quantity by considering half the bonding energy of the local electron density with all the system charge (because it is classical it includes the self-interaction of electrons) and half the bonding of the local nucleus with all other charge. The classical electrostatic interactions are hence treated in exactly the same manner as in the classical formula for the stress in a classical pair-potential system. The treatment of the classical electron-electron interaction differs only in that the electron is treated as a continuous distribution; this leads to the inclusion of self-interaction, which is absent in the case of force fields, being excluded by the “$\pi j$” exclusion on energy sums.

$$E_{\text{xc}}^i = \int d\mathbf{r} \left[ -\sum_{\alpha} \psi^i_\alpha \nabla^2 \psi^i_\alpha + \frac{1}{2} e^2 \phi \left[ n^i - \sum_j e^2 Z_j \frac{n^i}{|\mathbf{r} - \lambda \mathbf{R}_j|} + \varepsilon_{\text{xc}} \left( \frac{n^j}{2} \right) \right] + \frac{1}{2} \sum_{j \neq i} \frac{e^2 Z_i Z_j}{|\lambda \mathbf{R}_i - \lambda \mathbf{R}_j|} \right]$$

$$n^i = \lambda^{-3} n^i \left( \mathbf{r}/\lambda \right)$$

$$\psi^i = \lambda^{-3/2} \psi^i \left( \mathbf{r}/\lambda \right)$$

$$P_i = -\frac{dE_{\text{xc}}^i}{d\lambda} \left|_{\lambda=1} \right. \left( \frac{dV}{d\lambda} \right)^{-1} ; \quad dV = 3V_i$$

3. Procedure

Calculations were performed with the Locally Self-Consistent Multiple Scattering Method (LSMS) [10] on 9826 cores of Jaguar-PF, a high performance computer of the Oak Ridge Leadership Computing Facility. The electron multiple scattering includes atomic scattering up to $l=3$ for atoms within 7.5 a.u. and to $l=2$ out to 11.3 a.u. The local Kohn-Sham potential was treated in the Atomic Sphere Approximation [11]. We applied the LSMS to calculate the atomic level pressure of a 9826-
atom sample of alpha Fe after a PKA with a velocity in the [113] direction that corresponds to an impulse delivered by a 1 keV neutron. The sample was initially in equilibrium at a temperature of 100K, periodic boundary conditions were in effect, the pressure was maintained at zero, and the atoms moved according to embedded atom forces integrated with variable time steps to account for initially high atomic velocities [12]. Specifically, the MOLDY-MD code [13] was used with the force fields developed by Finnis and Sinclair [14] as modified by Calder and Bacon [2]. The LSMS calculations correspond to a time 3.6ps after the initial impact.

4. Distribution of volume and pressure
The variation of the local Voronoi polyhedron (VP) volumes is depicted in figure 2; sphere sizes indicate the difference in volume from the average; color also indicates the difference from the average, red is expanded and blue is contracted. Therefore, the sites with volume very close to that of the bulk appear as small white dots. At a particular instant of time the VP-volumes vary from site to site due to the thermal motion of the atoms; there are also significant changes in VP-volume at defects. Furthermore, the impulse from the cascade initiates a pressure wave that reflects from the periodic boundary conditions. Multiple reflections from the boundaries of our small cell result in modulation of the strain field over a length scale of many lattice spacings that results in the extended red and blue regions in the figure. In figure 3 the local pressure at each site is shown. The representation is identical to that of the VP-volumes; sites with pressure near zero appear as small white dots. Comparing figures 2 and 3 a correlation between volume and pressure can be seen.

![Figure 2. Deviation of VP-Volume from average value (79.5 a.u.).](image1)

![Figure 3. Deviation of local pressure from average value (in a.u.).](image2)

In figure 4 the VP-volumes appear correlated with the pressure in natural way, compressive (positive) pressure is associated with lower volume. Although the volumes at a particular pressure have considerable scatter, the maximum volume appears to be clearly demarked by a line, a line of critical volume as a function of pressure. For a given pressure the population of VP-volumes lies overwhelmingly below this line. Its slope defines a pseudo bulk modulus, \( B_c = -\frac{dP}{dV} \), of 134 GPa. By construction, the average derivative of pressure with respect to volume (multiplied by the negative of the volume) of all local pressures is the actual bulk modulus, \( B \). For comparison the volume versus pressure curve is shown for a perfect crystal of alpha iron at zero temperature calculated to the same level of approximation as the 9826-atom damage-sample. The perfect crystal line passes through the center of the distribution of points, showing that the average distribution of volumes as a function of
pressure in the damage-sample is reproduced approximately by volume versus pressure curve of the perfect crystalline-sample for most of the pressure range. The two line cross at low and high volumes. The high volumes on the critical line in the damage-sample have a smaller “compressibility” than the perfect crystal while those at low volume have a greater compressibility. It will be interesting, in further studies, to determine whether or not, under increased hydrostatic pressure, the sample as a whole responds mainly through a reduction of volume of sites at the critical volume.

Magnetic moments also decrease with pressure. This is a correlation that is affected through the volume; the bandwidth increases as the distance to neighbors is reduced, resulting in a smaller exchange splitting. Figure 5 shows the local moments as a function of pressure; for comparison the atomic moment in perfect bulk Fe calculated in exactly the same way is also shown. The bulk moment provides an upper bound to the moment at each pressure. The same relationship is found in plotting the moment versus volume (figure 6). The size of the local moment can be explained in part by the change in volume but other aspects of the local atomic environment are clearly important. We have not attempted to analyze the local moment in terms of local geometry other than the local volume. A clear next step is to correlate the moment with the local value of the overlapped “electron-density” evaluated with an Embedded Atom Method as was proposed by Dudarev [15].

5. Conclusions
We have briefly described first principles local stress and computed the local pressure for a sizable (9826 atom) model of a single time step in the evolution of a radiation cascade. We find the local pressure to be correlated with other local quantities in a way that is reasonable and aids in our understanding of connection between different local environments and local properties. We propose that the sensitivity of the local stress to the local atomic environment will lead to its expanded use in understanding materials behavior at the atom level. In this paper we have made comparisons only to the local pressure in perfect bulk iron. Planned further comparisons include, for example, to other time steps within the cascade and to the same size system but with thermal displacements only. Further comparisons with samples at other temperatures, ambient pressure, and with impurities will clarify the meaning of the local stresses and add to its utility as a descriptive tool.

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Figure 6. Local moments as a function of VP-volume; red line is the moment per atom in perfect crystal.

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