

Molecular dynamics simulations of irradiation defects in graphite: Single crystal mechanical and thermal properties



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ABSTRACT

Molecular dynamics simulations of single crystal graphite have been performed, incorporating point and extended defect structures formed as a result of thermally annealed radiation damage. These AIREBO potential calculations have simulated the changes to crystal dimensions, elastic moduli and thermal expansion due to the formation of different representative morphologies of extended irradiation-induced defects (vacancy and interstitial aggregates) and over a range of atomic displacement fractions. We find that, in addition to the simulation method reproducing the important mechanical and thermal properties of virgin graphite, the property changes caused by the formation of extended defects in the graphite crystal structure qualitatively agree with experimental observations at different irradiation/annealing temperature regimes. The results of these calculations provide a direct insight into how the underlying atomic scale defects and dislocations created by radiation damage can lead to material property changes, and demonstrate how this computationally efficient simulation method can be employed to reproduce crystallite changes in large-scale models of polygranular graphite.

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1. Introduction

A detailed understanding of the response of graphite to energetic particle irradiation, particularly when consisting of fast neutrons, is important to efforts to understand the performance and operational lifetimes of graphite moderated nuclear reactor cores [1]. Nuclear graphite, which acts as both a moderator and structural component in many currently operating gas cooled power reactors and also in planned next generation very high temperature reactors, is a largely isotropic bulk material at the macro scale which has several different levels of structural complexity over different length scales but is ultimately formed from individual crystallites [2–4]. These crystallites consist of layers of sp^2 bonded carbons, stacked according to the Bernal structure (AB stacking) [5], which have highly anisotropic physical properties due to the very strong bonds within the layers and the relatively weak interlayer binding. The effect that neutron irradiation has on these individual crystallites is to cause significant changes to their electrical, elastic and thermal properties [1,6]. Most strikingly, bulk dimensional changes occur: an expansion of the crystal in the c -direction (perpendicular to the layers) and a contraction in the a -direction (parallel to the layers) [7,8].

The effect that neutron irradiation has on graphite crystals has been studied extensively using samples of highly oriented pyrolytic graphite (HOPG) which enables these strongly anisotropic property changes to be observed on a macroscopic scale. Although HOPG is not a single crystal, the crystallites are arranged so that the misalignment of c axes between crystals is small (0.4–0.8 degrees depending on the grade [2]). Misalignments within the basal plane have limited effects, especially for harmonic properties like elastic constants which are isotropic in the basal plane. Detailed reviews of these experiments can be found in Refs. [1,9], but in general, the material property changes are found to be relatively insensitive to irradiation flux, but highly sensitive to temperature, usually with the higher temperatures reducing the extent of the changes. We note that a flux effect does exist for irradiations below 250 °C, because the rate of annealing of damage is comparable to the rate of damage – in this case for a given fluence, damage caused by a high flux is greater than damage from a low flux, since the latter has had a longer time to anneal. This gives rise to the concept of equivalent temperature for comparing in service and materials test reactor (MTR) data [1].

The underlying physical processes and mechanisms driving these changes to the crystal properties due to irradiation are still the subject of debate even after many decades of active research [9,10]. It is broadly accepted that the irradiation damage can be characterised by the creation and aggregation of large numbers

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of point defects which can then distort the surrounding lattice [1,9,11]. However there are substantial gaps in our understanding of how this population of defects is created, evolves and interacts, and crucially how this leads to the experimentally observed property changes. There are numerous experimental insights into extended defect formation in irradiated graphite, which can characterise both the kinetics of the evolution and the morphologies of extended defects. For example, high resolution transmission electron microscopy (HRTEM) images of irradiation damaged graphite have shown prismatic dislocation loops forming at higher temperatures, which are understood to form from the aggregation of interstitial atoms into new layers [12–14]. Recent HRTEM images of irradiated graphene layers with atomic resolution have also shown the formation of non-basal dislocations from vacancy aggregation into lines [15–17].

The effect that different densities and morphologies of both point defects and extended defects can have on the crystal properties can now be investigated with accurate and realistic atomistic models, thanks to modern computational resources. This can help create a quantitative link between atomic displacements and the observed material property changes. Developing an understanding of how different types and densities of defects result in different property changes can then help elucidate the mechanisms of the changes occurring to the real material as a result of the irradiation. In this paper, we describe large scale atomistic molecular dynamics simulations employing a reactive inter-atomic potential, of single crystal graphite with a range of displacement defect densities and morphologies. These morphologies consist of distributions of isolated interstitial atoms, non-basal dislocations loops (formed from vacancy coalescence) and distributions formed of prismatic dislocation loops (from interstitial coalescence). These morphologies correspond in principle to different stages in the thermal annealing of displacement damage. For each type of damage morphology, and over a range of densities, the bulk dimensional change, c -axis elastic constants and coefficient of thermal expansion (CTE) are calculated directly and without approximation using constant temperature and pressure molecular dynamics algorithms. The results of these calculations are then compared with relevant experimental observations. The plan of the rest of the paper is as follows: in the next section the methods employed are described in detail, along with a series of calculations on the properties of perfect graphite to validate the approach. In Section 3, the different models for defects in irradiation damaged graphite are explained and justified, along with details on how these atomic scale models are created. In Section 4, the results of the simulations of the property changes for the defect models are described in detail. Then, in the final section, a discussion of the results and conclusions are given.

2. Simulation methods

In order to accommodate extended defect structures and the long-range strains and distortions to the crystal structure induced by them, large simulation cells must be employed. In this work, an orthorhombic graphite simulation cell size of $10.7 \text{ nm} \times 10.7 \text{ nm} \times 5.4 \text{ nm}$ is used in all calculations, which contains 16 layers of 4400 carbon atoms each, giving 70,400 atoms in total (see Fig. 4(a)). Periodic boundary conditions are applied in all three directions.

To accurately model the graphite system, reproducing both mechanical properties and defect structures and energetics, and to enable the treatment of large systems with computational efficiency, the adaptive intermolecular reactive empirical bond order potential (AIREBO) for carbon is employed [18]. The AIREBO potential is an extension of the second-generation reactive empirical bond order potential (REBO) of Brenner [19], incorporating

inter-molecular interaction terms to correctly model the graphite inter-layer bonding and is considered a state-of-the-art potential in simulating graphitic systems [20,21]. This potential is implemented in the large-scale atomic/molecular massively parallel simulator (LAMMPS) molecular dynamics (MD) code, which incorporates a wide range of simulation algorithms [22]. The dynamical evolution of the system can be simulated in the canonical (NVT) or isothermal–isobaric (NPT) ensembles. The first of these integrates the thermal motion of the atoms in a fixed super-cell coupling to an external heat bath. The second of these, in addition to being coupled to an external heat bath, varies the simulation cell dimensions in order to maintain a constant pressure. The external pressure can be specified as either a scalar (hydrostatic) pressure (isobaric ensemble) or as components of a symmetric stress tensor (constant stress ensemble).

The equilibrium crystal dimensions are determined by optimising the atomic positions along with the three simulation cell lattice vectors independently with respect to the total system energy. For the perfect graphite crystal, the optimised c lattice parameter is 0.671 nm and the optimised a lattice parameter is 0.242 nm, which are consistent with experimental values [23]. To calculate the elastic constants of the simulation cell, the simulation box is deformed in each direction by a small fixed amount (0.1%) and the change in the stress tensor is measured. For the elastic moduli in the basal direction, the agreement with experiment is reasonably good ($C_{11} + C_{12}$ is 1300 GPa for AIREBO and 1240 GPa measured [24]), as is the elastic modulus in the c -direction (C_{33} is 38 GPa for AIREBO and 37 GPa measured). However, the shear modulus in the basal direction (C_{44}) is an order of magnitude smaller than the experimental result (0.3 GPa AIREBO and 5 GPa measured). This is due to energy differences for different layer stacking registries in graphite not being reproduced by the potential model, and is a well known problem with this and other pair potentials for layered materials [2,25]. We believe this anomalous behaviour will not profoundly affect the overall elastic response of the system to defect structures in the c -direction because both $C_{11} \gg C_{44}$ and $C_{33} \gg C_{44}$ still hold.

The linear thermal expansion of the system in each direction at any particular pressure or load can be calculated directly and without approximation by employing the isothermal–isobaric ensemble in the MD simulations at different temperatures and measuring the change in the time-averaged lattice vectors that result. This requires long-timescale MD runs in order to obtain converged averages at higher temperatures (100 ps to 1 ns). For perfect graphite, the linear expansion in both the a and c directions is shown in Fig. 1 from 0 K to 1000 K in intervals of 100 K. As has

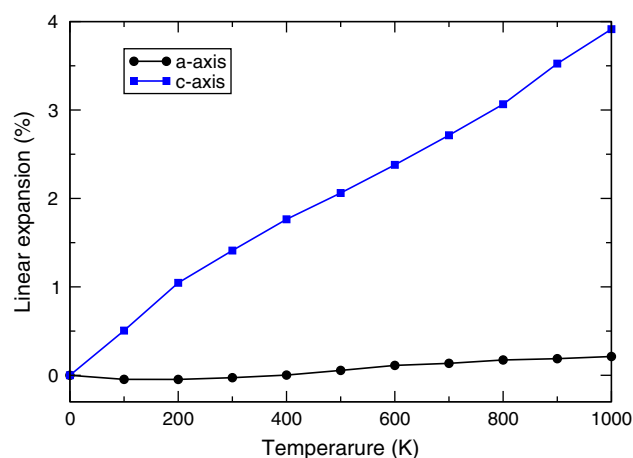


Fig. 1. Thermal expansion of graphite in the a - and c -directions calculated using the MD constant pressure method.

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