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# Thermal resistance from irradiation defects in graphite

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ABSTRACT

An atomistic level understanding of how varying types and numbers of irradiation induced defects affect thermal resistance in graphite is vital in designing accident tolerant fuels for next-generation nuclear reactors. To this end we performed equilibrium molecular dynamics simulations and computed the change to thermal conductivity due to a series of clustering and non-clustering point defects using the Green–Kubo method. In addition, we present a comprehensive discussion of several approaches to converge the integral of the heat current autocorrelation function. Our calculations show that more energetically favorable clustering defects exhibit fewer low frequency modes and increase the anisotropic nature of graphite selectively exerting a significant effect on thermal resistance along the *c*-axis.



## 1. Introduction

In the early 1940s, polycrystalline graphite was the only abundantly produced material with the required purity to be used as a moderator in nuclear reactors [1]. While other reactor materials have since been adopted, at the present time, graphite is still in high demand for the development of high-tech fuel elements for next-generation nuclear reactors. Graphite or pyrolytic carbon is included in nuclear fuel assemblies to encapsulate the fissile material. In these applications, in addition to utilizing its high temperature strength, the graphite acts as a neutron moderator and reflector. In some fuels graphite encapsulates the fissile materials in which case all the heat produced by fission in a fuel pin must be conducted out through the graphite. As the moderating properties of graphite are temperature dependent, accurately predicting the thermal conductivity of graphite and other fuel assembly materials—including how their thermal conductivity evolves under irradiation—is vitally important for the design of accident tolerant fuels.

The thermal conductivity ($\kappa$) of graphite is experimentally found to change with synthesis conditions and while in service as a direct result of radiation [2]. This indicates that $\kappa$ is not an intrinsic property and is instead governed by the defect morphology of the graphite. Simulations typically measure intrinsic properties, but we aim to determine an atomistic level understanding of scattering processes from collections of irradiation induced point defects and to establish a systematic understanding of how defect type, number and different defect-type ensembles affect thermal resistance and phonon mean free path in graphite. We do so with the goal that the insight that we gain can be incorporated into approaches for quantitatively predicting the lattice thermal conductivity that are based on solving the Boltzmann transport equation. Such a tool would be useful to nuclear engineers and materials scientists in the process of designing new reactors and fuel systems that are accident tolerant. As the first step along this path, we have computed the energy and structure of a zoo of point defects and determined their separate effects on thermal conductivity along and across the basal plane.

In Section 2 we establish and validate our method for computing thermal conductivity of defect-free graphite. More specifically, we discuss advantages and challenges associated with the Green–Kubo formalism: in Section 2.1 we discuss different approaches to converge the heat current autocorrelation function (HCACF) and propose a solution based on our findings; the issue of size convergence is explained and addressed in Section 2.2. After establishing an adequate system size, we introduce defects and compute their formation energies in Section 3. Values are obtained using classical molecular dynamics and compared with density functional theory (DFT) calculations. Interstitial defects are also annealed to find the most energetically favorable configuration. In Section 4 we compare the perfect crystalline system, where transport is limited by crystal lattice anharmonicity and the acoustic phonons carrying the bulk of heat are only scattered by other phonons, with systems with point defects, where defect scattering is expected to play a

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crucial role in thermal transport. Concluding remarks are presented in Section 5.

## 2. Computational method and validation

Molecular dynamics modeling captures the anharmonic interactions of atomic vibrations that carry heat and both equilibrium and non-equilibrium simulations can be used to predict thermal conductivity [3]. The Green–Kubo formalism [4,5] is a well established equilibrium molecular dynamics approach that has been used successfully to compute thermal conductivity in a wide range of materials from silicon [6] to metal–organic-frameworks [7]. This method is derived from the fluctuation–dissipation theorem and computes the thermal conductivity, $\kappa$, from the equilibrium fluctuations in the heat current vector, $\mathbf{J}$, by:

$$\kappa_{xx} = \frac{V}{k_B T^2} \int_0^\infty C_{\mathbf{J}xx}(\tau)\, d\tau, \tag{1}$$

where $k_B, T$ and $V$ are the Boltzmann's constant, temperature and volume of the simulated region respectively. The term $C_{\mathbf{J}}(\tau) = \langle \mathbf{J}(t)\mathbf{J}(t+\tau)\rangle$, and is the non-normalized heat current autocorrelation function (HCACF). The net flow of heat fluctuates about zero at equilibrium and the thermal conductivity is related to how long it takes for the fluctuations to dissipate. Both equilibrium and non-equilibrium molecular dynamics (NEMD) simulations suffer from size artifacts that must be mitigated. In NEMD, the simulated system size must be larger than the intrinsic mean-free path of the phonons in order to eliminate ballistic transport between the heat source and sink [3]. Equilibrium MD affords one a smaller system size as phonons may move through periodic boundaries unhindered.

Simulations were performed with the large-scale equilibrium classical molecular dynamics software LAMMPS [8]. After relaxing the atomic structure, along with the size of the compute cell, all systems were given a thermal energy equivalent to 300 K and equilibrated in the microcanonical ensemble (NVE) for 50 ps before starting to record the HCACF. The simulations were then performed for an additional 0.6 ns with a 0.2 fs time step and periodic boundary conditions. Throughout the period in NVE the average temperature remained at approximately 300 K. This is well below the Debye temperature for graphite (approximately 2500 K in the basal plane and 950 K along the *c*-axis [2]). However, our goal is a comparative analysis of phonon scattering from and around the defect. As scattering from classically occupied high frequency modes is present with and without the defect this has little contribution to the *change* in $\kappa$. The adaptive intermolecular reactive empirical bond-order (AIREBO) potential function formulated by Stuart et al. [9] was used for all simulations. The AIREBO potential includes anharmonic terms in the carbon bonds, an adaptive treatment of the non-bonded and dihedral angle interactions and has the capability to model the interaction between layers in graphite [9]. Two main challenges result from using the Green–Kubo: (1) determining an appropriate system size and (2) converging the HCACF. We shall first address the latter challenge and propose a solution based on the work of Chen et al. [10].

### 2.1. HCACF convergence

There is no average heat flux, $\langle \mathbf{J}\rangle$, for a system in equilibrium, and the HCACF, *i.e.* the term inside the integral in Eq. (1), is therefore expected to decay to zero given sufficient time. Instead, long lived oscillations with a significant contribution to the computed thermal conductivity have been observed [11–14]; this behavior is illustrated in Fig. 1. The HCACF is crucial in computing $\kappa$ using the Green–Kubo method and yet there is little consensus among researchers on whether these oscillations are significant to thermal transport or a result of noise, and as to what approach to take. A discussion of this behavior and of possible approaches to converging the HCACF is essential in understanding the limitations of the Green–Kubo formalism and validating thermal transport calculations.

Fig. 1(a) shows the accumulation of the averaged HCACF along a basal direction over a typical simulation. It can be seen that the tail of the HCACF contains many fluctuations, but rather than these decaying smoothly as more data is averaged there occur sporadic events that can overwhelm the average to add new fluctuations to $C_J(\tau)$ and significantly change the initial value $C_J(0)$. These large events show up in the majority of simulations and for all simulated system sizes. Long lasting oscillations are prevalent along the basal plane and are different from oscillations along the *c*-axis (see Fig. 1). Fluctuations along the *c*-axis exhibit a higher frequency and oscillate around zero with the HCACF converging to zero with only minor instabilities affecting its integral. Fluctuations along the basal plane, on the other hand, do not fade away during computation time and significantly affect $\kappa$. In graphite, $\kappa$ calculations in the *c*-direction are not affected by HCACF fluctuations as much as basal plane calculations are. This makes results perpendicular to the basal plane easier to compute and more reliable.

Along the basal plane the HCACF exhibits a two-stage decay: a rapid decay associated with high frequency phonons and a slower decay associated with lower frequency phonons. Similar two-stage decay (or three-stage decay) is observed in many single element materials and different authors have modeled $\kappa$ by fitting the HCACF to the sum of two or more exponentials [13–15]. This is a more physically meaningful approach than a single exponential fit in that it captures multiple relaxation processes, but it neglects the contribution of the HCACF tail, which results in a systematic underestimation of $\kappa$ [3,14]. When addressing the issue of convergence in the HCACF we have examined a wide variety of strategies. These strategies include direct integration of the HCACF truncated to various cutoffs, fits of varying sums of exponentials to the truncated HCACF, and fits in the frequency domain. Here we present only a few of the best or otherwise insightful findings and a brief discussion of our approach.

(i–iv) Direct numerical integration of the truncated HCACF up to (i) 50 ps along *z* and 20 ps along *x* and *y*, (ii) 5 ps, and (iii–iv) a noise dependent cut off time, $t_c$, proposed by Chen et al. and described below [10]. For (iv) individual cut-offs were computed for each HCACF as shown in Fig. 1(b)–(d), and for (iii) an average $t_c$ was used for each simulation set.

(v) Single exponential fits to the first 5 ps of the HCACF.

(vi) The fitting procedure proposed by Chen et al., which includes a fixed offset term in the fitting function:

$$\frac{C_{\mathbf{J}}(\tau)}{C_{\mathbf{J}}(0)} = A_1 e^{-\tau/t_1} + A_2 e^{-\tau/t_2} + Y_0, \tag{2}$$

such that $\kappa$ is computed as

$$\kappa_{xx} = \frac{V C_{\mathbf{J}xx}(0)}{k_B T^2}(A_1 t_1 + A_2 t_2 + Y_0 t_c), \tag{3}$$

where $A_1, A_2, Y_0, t_1$ and $t_2$ are fitting parameters. Chen et al. argue that including the offset $Y_0$ reduces the computational error. In our implementation of this we used the simplex method to optimize the fit variables. It is physically meaningless to have negative $Y_0$ and this term was weighed with a Heaviside function to prohibit negative $Y_0$ terms. We also imposed the condition that $A_1 + A_2 + Y_0 = 1$.

(vii) Double exponential of the form in (vi) with $Y_o$ set to zero.

(viii) Triple exponential of the form: