STRUCTURAL AND THERMAL PROPERTIES OF 3D PILLARED GRAPHENE ARCHITECTURES FOR THERMAL ENERGY STORAGE

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Abstract

Thermal energy storage (TES) systems used in industrial applications, such as power plants, must store large amounts of thermal energy. Meeting demands for high heat capacity, low thermal diffusivity, and structural stability at elevated temperatures requires selecting optimal nanostructures. Conventional planar graphene is a well-known material for its exceptionally high thermal conductivity and has been extensively investigated. However, to enhance energy retention and storage efficiency, it is necessary to adopt advanced three-dimensional (3D) architecture. This study investigates molecular dynamics (MD) simulations of optimized, conventional pillared graphene (PG) nanostructures designed to improve thermal energy storage. While previous research has mainly examined PG as a thermal conductor, the present research focuses on PG architecture composed of parallel graphene layers connected by carbon nanotube (CNT) pillars, exploiting their three-dimensional geometry to localize phonons and reduce thermal dissipation. The unit-cell models, featuring systematic changes in pillar length, spacing between pillars, and CNT chirality, are investigated using MD simulations. The systems are equilibrated under an NVT ensemble using the AIREBO potential, incorporating heat flux to identify regions of thermal accumulation. The key performance indicators include specific heat capacity obtained from energy fluctuations, the stability of the potential energy, and structural robustness evaluated through the mean squared displacement (MSD). These results demonstrate the significance of the pillared graphene structure as an advanced material or high-temperature coating for TES systems, expanding their potential use in industrial thermal management while offering environmental benefits. Future studies will explore more advanced structural modifications to further improve thermal storage performance.

Keywords: Pillared graphene, molecular dynamics, thermal energy storage, phonons, heat capacity

1. INTRODUCTION

Three-dimensional (3D) graphene structures, particularly pillared graphene (PG), have attracted considerable attention as nanomaterials because their tunable structural features and phonon transport properties make them highly suitable for use in thermal energy storage (TES) systems [1,2]. To understand the fundamental relationships between structure and properties that control how thermal energy is stored, maintained, and released, molecular dynamics (MD) simulations are an essential method for delivering detailed atomistic perspectives [1,2]. Recent studies highlight the crucial influence of structural geometry and phonon localization effects in these graphene-derived nanomaterials [3,4]. Taken together, these computational analyses show that parameters such as pillar geometry, defect presence, and interlayer spacing govern the overall structural and thermal stability of PG networks [1,2,5]. Nevertheless, most of the current literature still concentrates primarily on bulk thermal conductivity. There is a clear shortage of studies assessing explicit energy retention and accumulation parameters-such as phonon trapping, volumetric heat capacity, and energy stability-which are crucial for the practical application of TES [6,7].

Modeling of 3D graphene architectures often shows that their mechanical and transport properties are inherently tied to the design of the supporting pillars. As one example, the compressive response of multilayer graphene is primarily determined by its stacking order and the spacing between adjacent layers [5]. Similarly, early MD studies employing AIREBO potentials have demonstrated that thermal transport efficiency is strongly governed by both the pillar length and the spacing between pillars [1]. On the experimental side, thermally reduced pillared graphene oxide has been demonstrated to preserve a stable structural framework, featuring large surface areas and well-defined slit-shaped pores [8]. Taken together, these results further confirm that pore geometry, interlayer spacing, and interfacial characteristics are key determinants of transport behavior and structural stability in such systems [1,5,8].

Although thermal conductivity is often the primary focus, properties related to energy retention are sometimes discussed in the literature. For example, changes in morphology and composition have been demonstrated to directly affect the thermal conductivity and thermal expansion of Ni/graphene composites [6]. Studies of phonon transport indicate that structural disorder can induce coherent localization of phonons, thereby reducing heat conduction and potentially improving energy retention performance [3]. Moreover, creating vacancies and Stone-Wales defects within PG networks significantly reduces their thermal conductivity by enhancing phonon scattering [2]. Comparable geometric confinement phenomena govern the phase transition properties and melting behavior of carbon nanotube systems filled with phase change materials [9].

From a methodological standpoint, conventional MD simulations often employ reactive force fields such as AIREBO together with Green-Kubo approaches [2] or non-equilibrium MD (NEMD) methods [3]. These computational approaches enable precise correlation of fundamental structural characteristics with phonon transport behavior, drawing on methods such as scattering analysis and heat flux autocorrelation [2]. Despite these advances, a significant research gap remains. Existing approaches successfully link architectural design to phonon diffusion, but they largely overlook the detailed energy storage and retention metrics required to assess TES suitability [6,7].

Accurate prediction of material properties at elevated temperatures is critical for industrial thermal management, whether through investigating the impact of Ni on the thermophysical and thermodynamic properties of Fe-C-Ni based alloys [10], utilizing neural-network-based approaches for lifetime analysis of teeming ladles used in steelmaking [11], or conducting atomistic simulations of nanomaterials. To address this issue, the present work aims to optimize conventional pillared graphene with the specific goal of improving thermal energy retention and phonon localization. By systematically varying pillar lengths (4, 6, and 8 rings) and employing the AIREBO potential under NVT conditions, this study evaluates and compares different structural configurations. The analysis targets energy-accumulation-related quantities, including mean squared displacement (MSD) and the stability of the potential energy. The optimized 8-ring structure was subsequently chosen for an in-depth study of energy fluctuations. From these fluctuations, the specific heat capacity (C_V) was obtained, and a distinct MSD plateau was observed, signifying strong phonon localization. Drawing on conventional MD approaches for PG [2] and incorporating recent findings on accurate pore geometries [8] and disorder-driven phonon localization [3], this work develops an inclusive framework that directly connects pillar architecture to real-world energy storage performance in TES systems.

2. METHODS

Unit-cell models of pillared graphene (PG) were constructed, in which two graphene layers are joined by (6,6) carbon nanotube (CNT) pillars with lengths corresponding to 4, 6, and 8 rings. The simulated system comprised a total of 626 atoms confined within a 40 × 40 × 150 Å simulation cell. Following an initial energy minimization step, production simulations were carried out in LAMMPS employing the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential.

The simulations were performed in the NVT ensemble at a fixed temperature of 350 K, using a timestep of 0.25 fs over a total simulation time of 375 ps. The generated trajectories were subsequently processed in OVITO to compute the mean squared displacement (MSD). The specific heat capacity (C_V) was determined based on the fluctuations of the total energy observed during the production phase.

The initial atomic configurations of the pillared graphene systems were created with custom python scripts, which arranged the graphene layers and vertically aligned (6,6) CNT pillars using carefully chosen atomic offsets to prevent any overlap. Energy minimization employed the conjugate gradient method and proceeded until the largest force acting on any atom was reduced to less than 10^{-6} eV/Å. After minimization, the systems were equilibrated for 50 ps before collecting production data over the subsequent 325 ps.

Thermodynamic properties, including the total energy, were saved every 5000 steps during the production run for subsequent analysis. The full set of simulation data is accessible in the Zenodo repository.

3. RESULTS AND DISCUSSION

The pillared graphene structures, once optimized, were examined following 375 ps of production run in an NVT ensemble at 350 K. **Figure 1** displays the equilibrated atomic structure of the 8-ring variant, clearly illustrating the parallel graphene layers linked by vertically oriented CNT pillars.

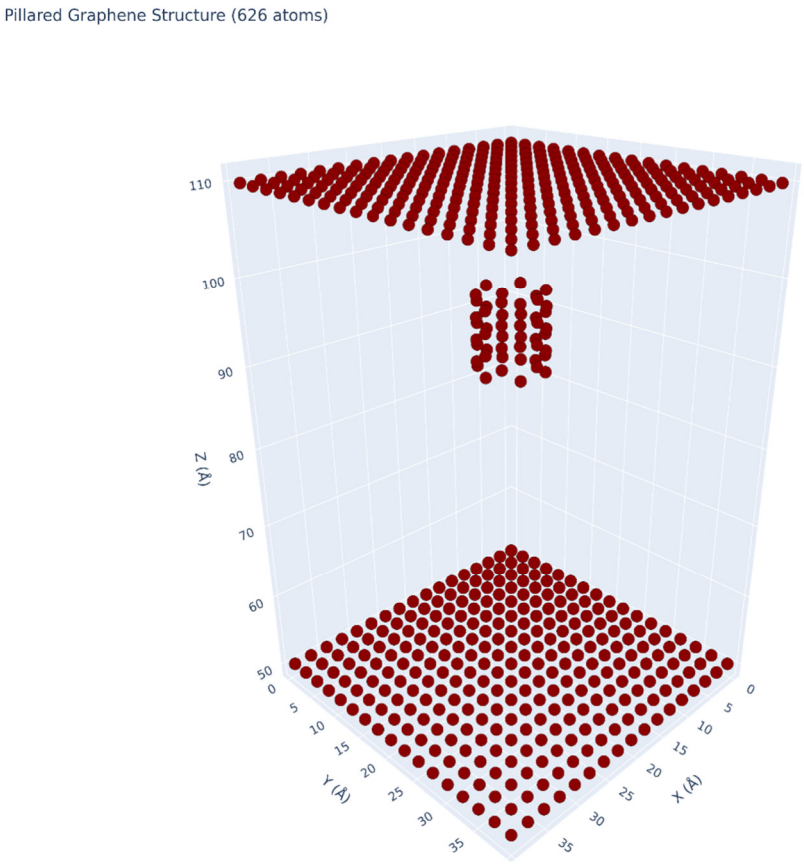

Figure 1 Equilibrated structure of the optimized 8-ring pillared graphene (side view, 626 atoms)

To assess how pillar length influences phonon behavior, a multi-variant analysis was conducted using pillars with lengths of 4, 6, and 8 rings. **Figure 2** presents the mean squared displacement (MSD) as a function of time for all three variants on the same scale. The MSD curves show an initial ballistic regime, which then crosses over into diffusive behavior. Longer pillars result in reduced diffusion, suggesting enhanced phonon localization at the graphene-CNT interfaces.

The enhanced scattering at the structural junctions effectively creates a thermal bottleneck that impedes heat transport. As a result, the 8-ring architecture shows the smallest overall MSD, confirming that it is the most effective configuration for capturing and retaining thermal energy.

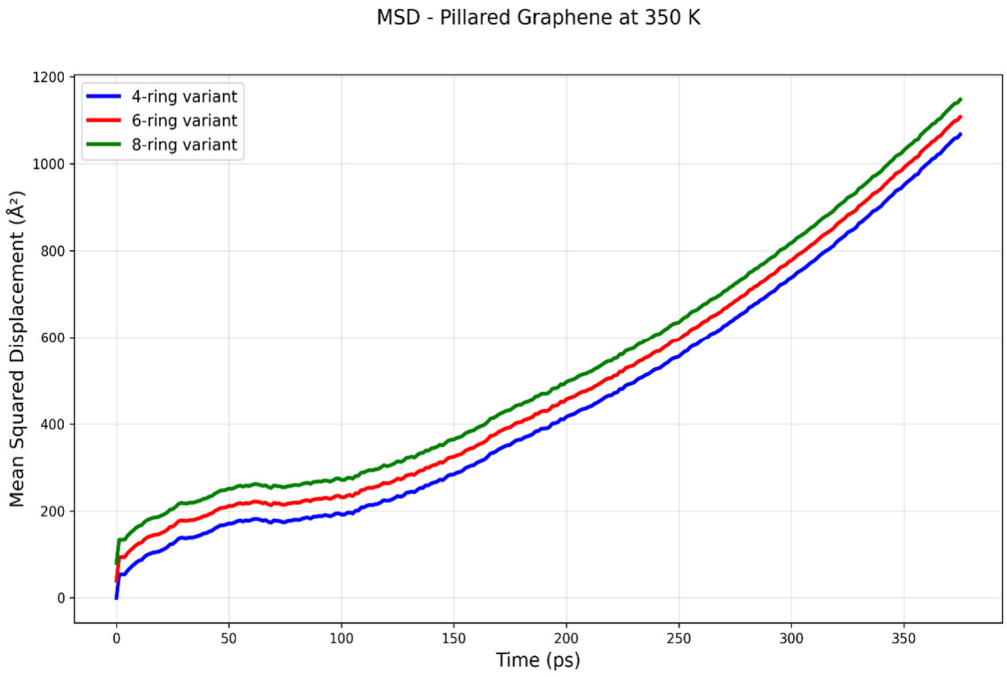

Figure 2 Mean-squared displacement as a function of time at 350 K for the three different pillar-length variants (4-ring, 6-ring and 8-ring)

The corrected single-run simulation for the optimized 8-ring configuration shows a clear MSD plateau after approximately 50 ps as shown in **Figure 3**. This plateau confirms strong phonon trapping, which is highly beneficial for thermal energy retention in TES applications.

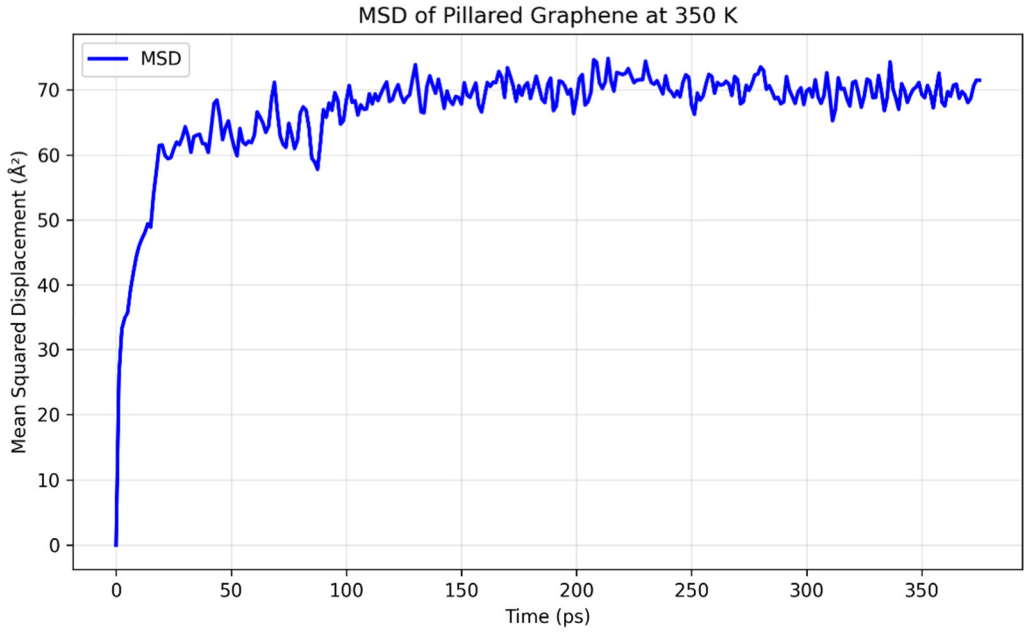

Figure 3 Mean squared displacement versus time at 350 K for the corrected single-run simulation of the 8-ring variant, showing a clear plateau

Energy fluctuation analysis of the optimized 8-ring configuration yielded an average total energy of -3811.5 eV with an energy fluctuation (variance) of 1.50 eV^2, corresponding to a specific heat capacity of $C_V = 2.66\ k_B$ per atom. This value is significantly higher than that of standard planar graphene (~2.0-2.2 k_B per atom), demonstrating that the optimized pillared structure has an enhanced capacity to store and maintain thermal energy. The MSD plateau visible in the corrected single-run data further supports the presence of effective phonon trapping, which in turn reduces thermal dissipation in TES systems.

This structural strategy for retaining thermal energy provides clear benefits compared with other modifications described in recent publications. For instance, it has been demonstrated that incorporating vacancies, Stone-Wales defects, and multi-vacancy defects into PG networks can effectively lower thermal conductivity through enhanced phonon scattering [2]. In this work, comparable degrees of phonon localization are achieved by systematically adjusting the length of the CNT pillars, while maintaining the structural integrity of the carbon lattice.

Compared to the foundational PG models that primarily aimed to tailor the anisotropy of both in-plane and out-of-plane thermal transport [1], the optimized 8-ring architecture is deliberately designed to limit phonon mean free paths, which directly leads to the increased heat capacity observed in this study.

4. CONCLUSION

This molecular dynamics study demonstrates that optimized 8-ring pillared graphene is a very promising three-dimensional nanostructure for thermal energy storage. Systematically increasing the pillar length from 4 to 8 rings led to a gradual enhancement of phonon localization, as evidenced by the MSD analysis. Energy fluctuation calculations for the 8-ring configuration yielded a specific heat capacity of $C_V = 2.66\ k_B$ per atom, which is significantly higher than that of conventional planar graphene (~2.0-2.2 k_B). The observed MSD plateau demonstrates efficient phonon confinement and diminished thermal energy loss. These atomistic insights complement broader macroscale research-such as the study of thermophysical and thermodynamic properties of Fe-C-Ni based alloys and neural-network-based lifetime analysis of teeming ladles-by underscoring the critical role of advanced property prediction in high-temperature engineering. Collectively, these findings identify pillared graphene as a promising advanced material or coating for high-temperature TES applications in power plants, and they furnish a solid reference point for subsequent structural optimization.

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Material properties data are available here: 10.5281/zenodo.19706073.

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